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ROCKET PROPELLANTS
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Cleveland, Ohio

Principal Investigators

J. C. Orth, Project Leader
R. E. Chute
S. Matsuda
W. H. Power
J. O. Smith
T. J. Wolanski

Technical Management

NASA-Lewis Research Center
APGO-Robert B. King

MONSANTO RESEARCH CORPORATION
BOSTON LABORATORY
Everett, Massachusetts 02149
Telephone: 617-389-0480

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I. INTRODUCTION

A. OBJECTIVE

This report describes the second stage of an investigation whose ultimate aims are to develop a fuel cell operating on storable reactants and to design a fuel cell that will operate relatively efficiently on a variety of fuels and oxidants.

During the first six months' work on the first phase of this project, the anodic oxidation of storable fuels and the cathodic reduction of storable oxidants were studied. After basic data from half-cell experiments were obtained, preliminary work on the construction and operation of complete cells was started.

The fabrication of cells has progressed to the point of combining certain systems such as hydrazine-palladium membrane-hydrogen peroxide or hydrazine-porous diffusion electrode-oxygen. Electrodes for such systems are being scaled up to three inches by three inches. Systems using nitric acid and dinitrogen tetroxide are being studied with smaller electrodes to obtain basic information before scaling up to the larger cell size. Hydrogen and hydrazine are the only rocket fuels regarded as usable directly in fuel cells. Although some supporting half-cell testing is still being done, emphasis is being placed on work with complete cells.

The anodic oxidation of hydrazine and the cathodic reduction of chlorine trifluoride (CTF) in anhydrous hydrogen fluoride (AHF) were demonstrated during the first six months work on this project. Current densities up to 5 ma/cm² were attained at solid carbon anodes in 1M hydrazine at 0.5 v polarization and at 3°C. Current densities as high as 20 ma/cm² were attained during the cathodic reduction of CTF in AHF. Current densities up to 100 ma/cm² at solid platinum anodes were attained with 1M hydrazine in a molten solution of KF·3HF at 85°C and at an anodic polarization of 0.5 v. Cathodic current densities of 5 ma/cm² were demonstrated in the same electrolyte at 85°C.

The present nonaqueous program is concerned with improving the above current-voltage relations by the use of flow-through porous electrodes. An associated problem is selection of materials of construction that will withstand the corrosive action of CTF in AHF solutions.

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B. SCOPE OF THIS REPORT

This report describes a systematic study of the solid palladium diffusion electrode, including pretreatments (heat treatment and catalyst deposition) that are required for using the palladium foil for transporting and anodically oxidizing hydrogen. The use of hydrazine as a fuel for supplying hydrogen to the palladium foil anode is also described.

The use of a porous Teflon diffusion electrode for the anodic oxidation of hydrogen or hydrazine and also for the cathodic reduction of oxygen and hydrogen peroxide is described. Such electrodes are combined for initial construction and demonstration of full-cell systems. Construction details for a full cell with 3-inch by 3-inch electrodes are described.

Polarization data are given for the anodic oxidation of hydrogen and hydrazine at flow-through electrodes and solid palladium foils in the anhydrous hydrogen fluoride system. *autho*

II. SUMMARY

A. AQUEOUS SYSTEMS

Full cells using hydrogen or hydrazine as fuels and oxygen or hydrogen peroxide as oxidants were constructed. Cathodes were fabricated from 3 by 3 inch nickel plaque, and hydrogen diffusion anodes were constructed from solid palladium membranes. Short-term discharge characteristics at 90°C were as follows:

<u>System</u>	<u>ma/cm²</u>	<u>Cell Voltage</u>
H ₂ -O ₂	50	0.60
N ₂ H ₄ -O ₂	55	0.65
N ₂ H ₄ -H ₂ O ₂	100	0.40

A full cell with a porous Teflon cathode and oxygen or 30% hydrogen peroxide as the oxidant coupled with a rhodium-catalyzed palladium diffusion anode with 85% hydrazine hydrate as the fuel and 5M KOH as the electrolyte was constructed and tested at 50°C. A cell voltage of 0.70 volt at 40 ma/cm² represents a promising start in full cell development.

Solid palladium-hydrogen diffusion electrodes were demonstrated for the use of 85% hydrazine hydrate as a fuel and 5M sulfuric acid as the electrolyte. Precipitation of hydrazine sulfate was prevented by the impermeability to hydrazine of the palladized palladium foil. Current densities of 40 ma/cm² at a polarization of 0.11 volt were attained at 30°C, 280 ma/cm² at 0.14 volt at 60°C, and 280 ma/cm² at 0.08 volt at 90°C.

The anodic oxidation of hydrogen produced by hydrazine hydrate catalytic decomposition was demonstrated at porous Teflon electrodes with 5M sulfuric acid electrolyte. A current density of 200 ma/cm² at a polarization of 0.16 volt was attained at 30°C.

Reproducible anodic polarization curves for palladium-silver hydrogen diffusion electrodes were obtained only after controlled oxidation of the surface of the foil. The palladium oxide film is an essential catalyst for the transfer and oxidation of hydrogen.

The oxide coating formed at 700°C after full annealing at 850°C resulted in the best anodic polarization for the palladium-silver electrode, particularly at high current densities (200 ma/cm² at 0.30 v polarization at 90°C).

Thick oxide films formed by temperature cycling did not improve electrode characteristics. Polarization was actually more severe at high current densities for the thick oxide electrodes than for thin oxide anodes.

Rhodium plating on the electrolyte side of the palladium-silver foil improved the electrode performance only if the foil was oxidized after plating, probably because of oxide reduction during the plating operation. Heat treating foils in a hydrogen atmosphere degraded the electrodes by reducing the palladium oxide catalytic film.

B. NONAQUEOUS SYSTEMS

The use of a solid palladium membrane as a hydrogen diffusion anode with hydrazine as a fuel was demonstrated in anhydrous hydrogen fluoride solution (KF·3HF) at 85°C. An anodic polarization of 39 ma/cm² was sustained with a polarization of 0.27 volt from the open-circuit potential. The solid palladium diffusion anode is of interest in the hydrogen fluoride system because of the separation of fuel (hydrazine) and oxidant (chlorine trifluoride) provided by the solid anode barrier. Mixing of unreacted fuel and oxidant in the electrolyte compartment will degrade the cell and will constitute a possible explosion hazard.

Porous nickel plaque has been demonstrated as a flow-through hydrogen electrode in KF·3HF at 85°C. A current density of 39 ma/cm² at a polarization of 0.20 volt from the reversible hydrogen potential was attained. This type of anode will be a candidate for a full-cell anode if provisions for preventing mixing of fuel and oxidant in the electrolyte compartment can be made.

III. PALLADIUM DIFFUSION ELECTRODE

A. BACKGROUND

1. General

The solid palladium hydrogen diffusion electrode is attractive for fuel cell systems using hydrogen gas or materials that can be converted to hydrogen gas. The palladium membrane not only provides an electrically conducting electrode but also can absorb and transfer hydrogen (and only hydrogen) from one surface to the opposite surface for use as an anode fuel. All materials other than hydrogen do not penetrate, so such soluble fuels as hydrazine can be restricted from the electrolyte compartment where they could diffuse to and degrade the cathode.

When dissolved in palladium, hydrogen is said to exist in the ionized state and, under the influence of an electrical field, the proton will be ejected from the metal. Hence, a mechanism is established for emitting a proton in an already ionized state, the essential step, $H = H^+ + e^-$, being produced within the metal (ref. 1). In contact with hydrogen gas at one atmosphere, palladium is known to absorb hydrogen until the ratio of hydrogen to palladium becomes 0.69, after which the electrode is in equilibrium with hydrogen gas at one atmosphere. The potential of this saturated palladium electrode will be the same as that of a reversible hydrogen electrode in contact with the same solution. Hoare and Schuldiner (ref. 2) have found that the palladium-hydrogen electrode has a potential plateau that is 50 millivolts more positive than the reversible hydrogen potential at H/Pd ratios of 0.03 to ratios approaching the saturation ratio of 0.69 when the reversible hydrogen potential is attained.

Oswin and Chodosh (ref. 3) have reported the use of nonporous palladium as a hydrogen anode when placed in contact with hydrogen gas on one side and an electrolyte on the reverse side. These authors indicate that some special surface pretreatment is required before high current densities can be drawn from the hydrogen-palladium anode, but they do not disclose the nature of this pretreatment.

Palladium-25% silver foils are preferred to pure palladium for use as active anodes, since the silver alloys do not expand and contract as severely as pure palladium during hydrogen cycling. This expansion and contraction can cause membrane cracking and failure (ref. 4).

A number of previous workers reported that heat treatment of palladium foil in air at elevated temperature increased the rate of diffusion of hydrogen through the foil (ref. 5) and improved its characteristics as a nonporous anode (ref. 6). The data, however, were rather qualitative, and the optimum condition for the treatment was not given in any of these papers. Also, the mechanism has not yet been clarified. A program is underway here to define optimum conditions for the heat treatment and to clarify the mechanism associated with the hydrogen diffusion nonporous electrode.

Although many factors could be related to the palladium heat treatment, the main effects on the characteristics of hydrogen diffusion electrodes are attributed to a change of crystal structure of the alloy and to a change of its surface properties, since heating in air up to 790°C will definitely form an oxide layer on the palladium surface. The effect of plating other elements on the palladium surface also should be considered.

As a nonporous diffusion anode, the palladium membrane is involved in three major reactions: (1) an interfacial reaction with hydrogen fuel involving adsorption and dissociation of hydrogen molecules into atomic hydrogen, or, very likely, protons (for simplicity the term "atomic hydrogen" will be used in this report); (2) diffusion of atomic hydrogen through the membrane; and (3) electrode reaction to release hydrogen atoms into ions at the electrolyte interface. It is most likely that all three reactions will be more or less affected by metallurgical factors resulting from the heat treatment at elevated temperatures.

2. Crystal Structure

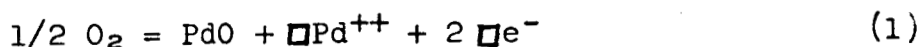
Since the very thin foil is severely cold rolled in the manufacturing process, heating to 600°C, which was previously recommended (ref. 5, 6) may give some recrystallization in addition to a full degree of recovery from the cold work. Heat treatment at 850°C is considered to be an optimum condition for the full annealing of palladium-silver alloys (ref. 7). Different metallurgical structures obtained by various heat treatment probably affect the properties of the membrane through the following mechanisms:

- (1) Different rate and amounts of molecular hydrogen may be adsorbed on the surface of cold rolled palladium and annealed palladium, because a preferred orientation on the surface of severely cold rolled palladium is possible.

- (2) Severe deformation of the alloy crystal structure by cold rolling will decrease the rate and the amount of absorption and diffusion of atomic hydrogen, since hydrogen atoms are absorbed into and diffused through interstitial sites of the palladium crystal lattice.
- (3) Fine-grained palladium will absorb more atomic hydrogen than coarse-grained material, since grain boundaries are expected to act as a sink for hydrogen atoms.
- (4) The diffusion rate of atomic hydrogen in fine-grained palladium will probably be faster than that in coarse-grained palladium, since boundary diffusion is much faster than bulk diffusion.
- (5) The effect of cold working and crystal structure on the anodic oxidation of atomic hydrogen to hydrogen ions cannot be predicted, although tensile stress in a metal is known to make it anodic to unstressed metal (ref. 8).

3. Oxide Film Formation

Palladium oxidizes readily in an oxygen atmosphere to form a visible oxide layer at 350 to 790°C (ref. 9). In this temperature range only palladium oxide is expected to form on a palladium-silver alloy because of the unstability of silver oxide. Palladium monoxide (PdO), the only known oxide of palladium at high temperature, is a p-type semiconductor (cation vacancy type) (ref. 10). Its cation-vacancy structure can be characterized by palladium ion vacancies, $\square\text{Pd}^{++}$, and simultaneous electron deficits, $\square\text{e}^-$, according to the following equation:



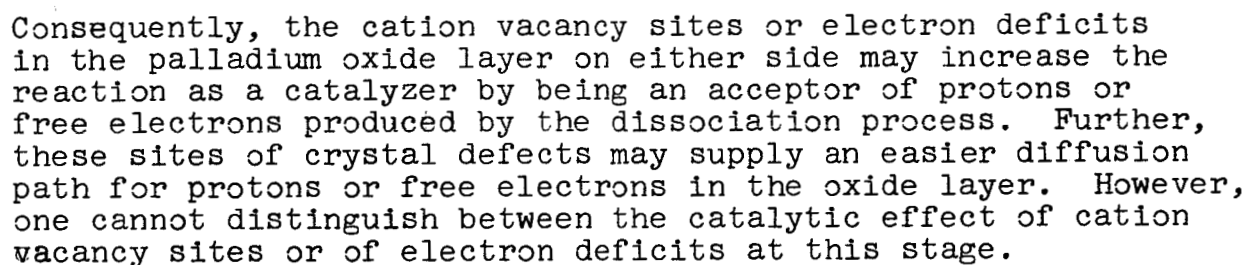
Assuming that no other major disorder equilibria are present, i.e., that the concentration of the cation vacancies is one half of the concentration of electron deficits, then the ideal mass action law can be expressed as follows:

$$\frac{c(\square\text{Pd}^{++}) \times c(\square\text{e}^-)^2}{(\text{PO}_2)^{1/2}} = K \quad \text{or}$$

$$c(\square\text{Pd}^{++}) = \frac{1}{2} c(\square\text{e}^-) = K' (\text{PO}_2)^{1/6} \quad (2)$$

where $K' = \left(\frac{K}{4}\right)^{1/3}$

On the other hand, we may assume that the transfer of hydrogen molecules into hydrogen ions can be represented as follows:



The concentration of cation vacancies will be increased by (1) increasing the oxygen pressure according to Equation (2), and (2) adding higher valency cations (which will result in decreasing the concentration ratio of electron deficits to cation vacancies, however). The addition of lower valency cations will decrease the concentration of cation vacancies and simultaneously increase the concentration ratio of electron deficits to cation vacancies.

1. Determination of Impurities in Palladium

*Model JxA-3A by Japan Electron-optics Laboratory, Tokyo, Japan

Then a quantitative analysis with the highest sensitivity of the instrument was performed for specific impurities, particularly those which would presumably affect the palladium-silver electrode performance.

Results of the quantitative analyses are shown in Table 1. Each value is the average of two samples. The analyses showed that the foil that was reduced by the "booking" process (rolling between copper plates) had three times the copper content of that rolled directly by a cluster rolling mill. Since copper forms a continuous series of solid solutions with palladium and silver, it is reasonable to assume that copper from the supporting plates diffused into the alloy during the rolling process.

Table 1
IMPURITIES IN PALLADIUM-25% SILVER FOIL

Manufacturing Process	<u>Impurity Content, %</u>			
	<u>Fe</u>	<u>Cu</u>	<u>Ni</u>	<u>Pb</u>
Booking	0.02	0.11	0.00	0.06
Cluster Rolling Mill	0.02	0.04	0.00	0.08

2. Effect of Heat Treatment on Metallographic Structure of the Palladium-25% Silver Foil

The metallographic structure of a cross section of palladium-25% silver foil as received from the manufacturer* is shown in Figure 1. All crystal grains were thoroughly destroyed during cold rolling and were severely deformed into an almost lamellar structure.

The structure of a foil after annealing in air for 5 hours at 850°C and quenching in water at room temperature is shown in Figure 2. The alloy had not only fully recovered after the heat treatment but also was highly crystalline, probably because of previous severe cold work. However, the grain sizes were extremely small because of a very high rate of nucleation. Since palladium monoxide decomposes at 790°C, no oxide film is formed at 850°C.

*J. Bishop Company.



Figure 1. Pd-25% Ag Foil as Received. 350X



Figure 2. Pd-25% Ag Foil Heat Treated in Air 2 Hr at 500°C. 350X



Figure 3. Pd-25% Ag Foil Heat Treated in Air 2 Hr at 600°C. 350X

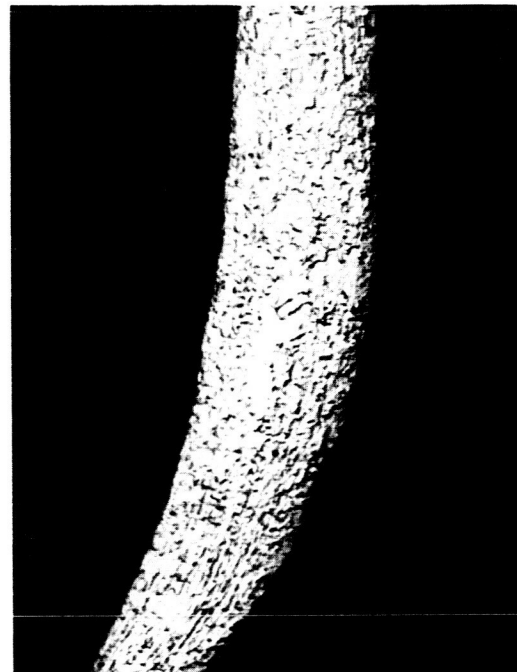


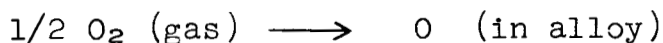
Figure 4. Pd-25% Ag Foil Heat Treated in Air 2 Hr at 700°C. 350X

The structure of a foil after annealing in air for five hours at 850°C, subsequently oxidizing in air for 2 hours at 700°C, and finally cooling in air is shown in Figure 3. The structure was essentially identical to that of the foil that was annealed only, shown in Figure 2.

The structures of the foils after heat treatment in air for two hours at 700, 600, and 500°C (without preheating at 850°C) are shown in Figures 4, 5, and 6, respectively. The photographs clearly indicate that some recrystallization occurred at the middle of the foil at 700°C, less at 600°C, and almost none at 500°C.

The structure of a foil that was heat treated in purified hydrogen gas for three hours at 600°C is shown in Figure 7. The hydrogen gas was purified before being introduced into the furnace by passing over fine copper foil heated at 450°C. The photograph shows that the alloy was recrystallized into a very uniform structure of palladium-silver-hydrogen solid solution as hydrogen diffused into and saturated the foil.

Heating a palladium-silver foil in air for two hours at 600°C and then in purified hydrogen for three hours at 600°C resulted in the structure shown in Figure 8. The surface of the heat treated foil appeared very bumpy and blistered. Except for a much smaller grain size in some areas of the foil, the structure was similar to that shown in Figure 7. The previous heat treatment in air introduced dissolved oxygen into the structure, following the reaction



We believe that hydrogen diffused into the alloy and formed water vapor by reacting with the dissolved oxygen. The water vapor eventually escaped from the alloy (explaining the blistered appearance) but hindered somewhat the grain growth of the palladium-silver-hydrogen solid solution, resulting in smaller grain sizes in some areas.

3. Surface Film Formed by Oxidation

Electron diffraction patterns* were taken by reflection from the surface of palladium-silver foils that had been heat treated in various manners. The foil that had been annealed at 850°C and quenched in water showed no evidence of an oxide film. Although

*Electron-microscope model JEM-6C by Japan Electron-optics Laboratory, Tokyo, Japan

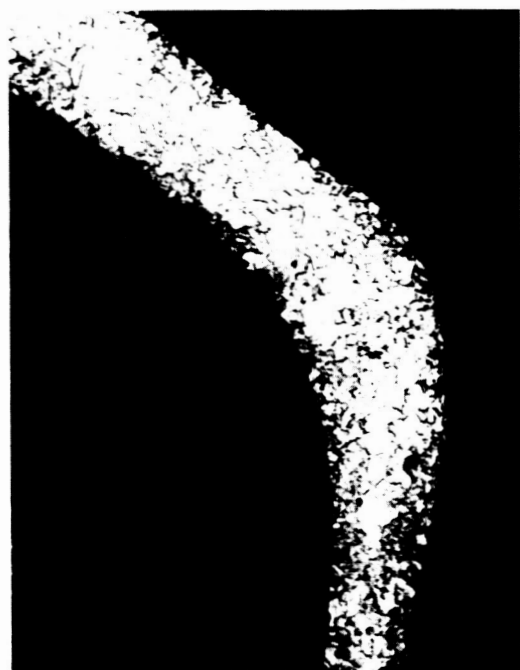


Figure 5. Pd-25% Ag Foil Heat
Treated in Air 5 Hr
at 850°C. 350X



Figure 6. Pd-25% Ag Foil Heat
Treated in Air 5 Hr
at 850°C and 2 Hr at
700°C. 350X

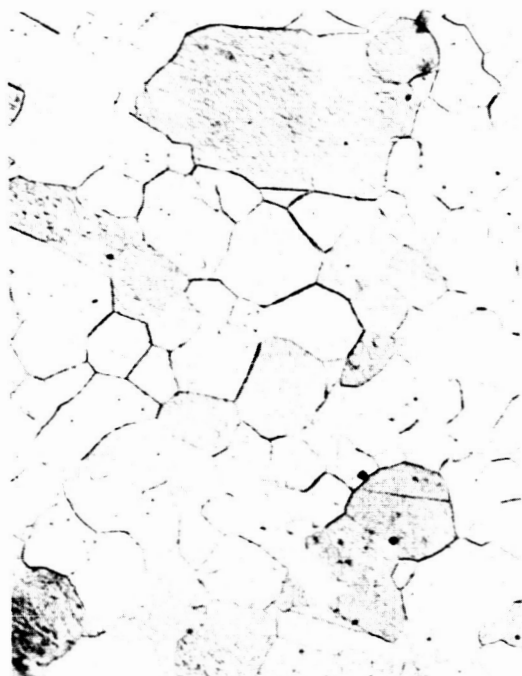


Figure 7. Pd-25% Ag Foil Heat
Treated in H₂ 3 Hr at
600°C. 350X

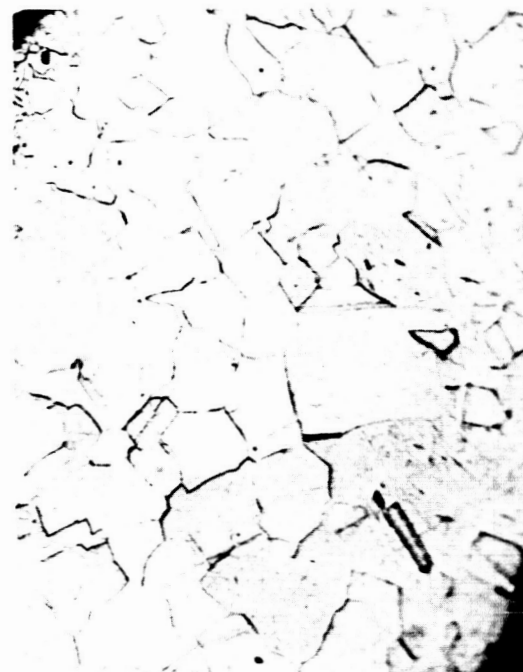


Figure 8. Pd-25% Ag Foil Heat
Treated in Air 2 Hr and
in H₂ 3 Hr at 600°C.
350X

some palladium oxide film would be expected to form, even during a rapid cooling, the film was apparently too thin to be detected by electron diffraction. The foil was shiny in appearance after heating and quenching.

Heating in air between 500°C and 700°C formed a palladium oxide coating of various thicknesses. The film had the crystal pattern of palladium monoxide. The surface of the foil heated at 700°C appeared greyish blue, at 600°C appeared slightly reddish blue, and at 500°C appeared deep blue. No palladium monoxide was detected by electron diffraction examination of a foil that was heat treated in air at 650°C and that was subsequently used as a hydrogen diffusion electrode until the foil lost its capacity as an anode. The disappearance of the oxide film was attributed to reduction by absorbed hydrogen (either atomic or proton), which is a potent reducing agent.

4. Effect of Heat Treatment on Polarization of Palladium-25% Silver Diffusion Electrode

The effect of the structure of palladium-25% silver foil on its capacity as an anode was determined by examining anodic polarization characteristics of heat treated foils. The polarization cell is shown in Figure 9. All electrodes were cleaned by immersing for 30 minutes in hot concentrated sulfuric acid saturated with chromic acid and washing in distilled water before heat treatment. Electrodes were kept in a desiccator after the cleaning process to avoid surface contamination from the atmosphere.

Full annealing was accomplished by heating the foil in air for five hours at 850°C and quenching in cold water to minimize oxide formation during cooling. The oxide film on the surface was formed by heating the foil in air for two hours at a given temperature and cooling in air.

Hydrogen was generated on the palladium-silver electrode surface in the left compartment by passing a constant current between the electrodes A and B. After saturating the electrode with hydrogen for 45 minutes, the cathodic treatment on the left side was continued at constant current while the right side of B was anodized against counter electrode C. Absorbed hydrogen then diffused through the foil and was discharged from the electrode surface in the right compartment. The anode potential was measured against a saturated calomel electrode (SCE) via a Luggin capillary, which was always placed at the same distance, 1 mm, from the electrode surface so that proper correction could be made for the IR drop between the anode and the tip of the Luggin capillary. At each of three different generating current densities between electrodes A and B, namely, 4, 40, and 250 ma/cm², the electrode potentials were measured

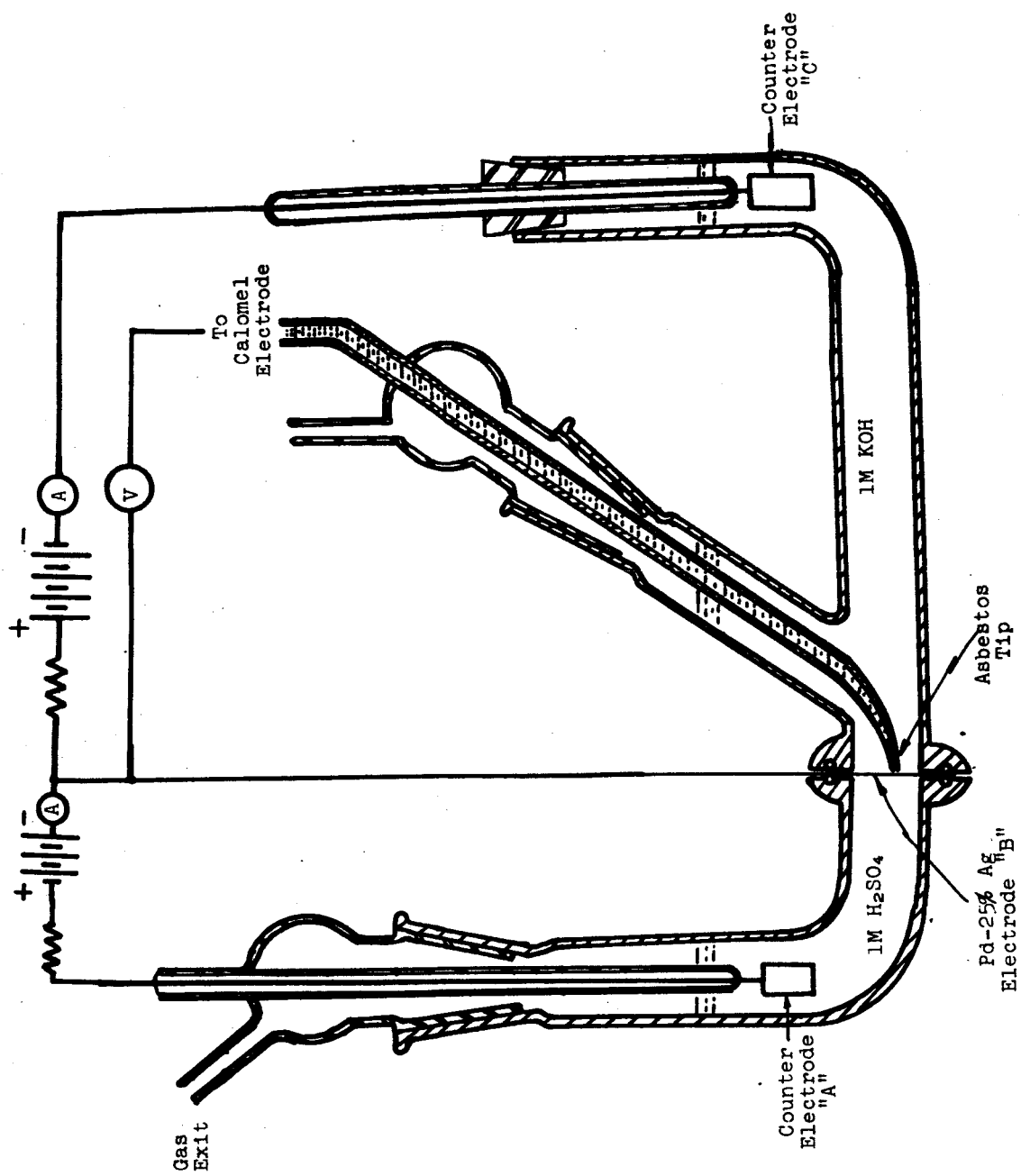


Figure 9. Polarization Cell Assembly

at various current densities between electrodes B and C to determine the anodic polarization characteristics of the electrode. Potentials were corrected for IR drop by selecting a value of R such that the log I vs potential relation was linear at current densities below the limiting current. All polarization tests were run at 90°C. Potentials in Table 2 have been calculated in relation to a reversible hydrogen electrode at the same pH and temperature as the test solutions.

The effects of annealing and oxidizing at several temperatures on the anodic polarization characteristics of palladium-silver foils are summarized in the following paragraphs.

a. Effect of Annealing Only

Annealing a palladium-silver foil above the decomposition temperature of palladium monoxide (790°C) and subsequent quenching to prevent oxidation resulted in non-reproducible anodic polarization characteristics (Tests 2a and 2b, Table 2). Polarization Test 2a was considerably better than that for the untreated foil (Test 1), while Test 2b was not as good as that of the untreated foil. Subsequent experiments have shown that controlled oxidation of the annealed foil is required for reproducibly good anodic polarization characteristics. Slightly different amounts of oxide film formed on electrodes 2a and 2b probably account for the considerable difference in discharge behavior.

b. Effect of Annealing and Oxidizing

Annealing at 850°C followed by oxidation in air at 700, 650, 600, and 500°C were the heat treatments for palladium-silver foils in Tests 3 through 6, Table 2. All in this series showed better anodic polarization characteristics than Tests 1, 2a, or 2b involving the foil as received or with annealing only and no oxidation. The foil that was oxidized at the highest temperature (700°C) (Test 3), showed the best anodic properties. This may be attributed to the higher number of cation vacancies in the oxide film formed by oxidation at the higher temperature. The other foils of this series (Tests 4 through 6) were oxidized at lower temperatures down to 500°C and were all strong anodes although somewhat less effective than the foil oxidized at the highest temperature (Test 3).

c. Effect of Oxidizing Only

Palladium-silver foils were oxidized at temperatures below the decomposition temperature of palladium monoxide in Tests 7 through 10.

Electrode Potential vs Hydrogen Electrode at same pH
and Temperature
Electrolyte - 1M KOH; Fuel - Hydrogen Cathodically Generated
in 1M H₂SO₄; Temperature - 90°C

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Of the oxidation temperatures chosen, 700, 650, 600, and 500°C, the best anode was oxidized at 600°C. The reason for this maximum performance at an intermediate temperature with the anodic properties decreasing as the temperature rises or falls is not yet clear. It is noted, however, that the electrodes, fully annealed before oxidation (Tests 3 through 6), had, in general, better polarization curves than those without previous full annealing (Tests 7 through 10). These tests will be rerun to check the reproducibility of the polarization curves. Poor reproducibility might be expected because of a possible nonreproducible structure change in the interior of the foil besides the formation of the oxide on the surface.

d. Effect of Temperature Cycling

The electrode for Test 11 was repeatedly heated for one hour at 650°C and cooled in liquid air. After the third heating, the foil was cooled in air to room temperature. No scaling was observed during the operation, and the electrode surface was greyish, indicating that a much thicker oxide film was formed than for the previous electrodes. The anodic polarization test for Test 11 was not as good as that for Test 8 (a single heating at 650°C for 2 hours), particularly at higher current densities.

5. Effect of Additional Plating

Since previous work in this laboratory showed that rhodium plating improved the performance of untreated palladium-silver diffusion electrodes, a series of experiments was performed to determine more definitely the effect of rhodium plating. The cell used was similar to that shown in Figure 9 except that pure hydrogen gas was directly supplied as a fuel to the left compartment, and 5M potassium hydroxide was used as an electrolyte in the right compartment. The hydrogen gas was purified by passing through a cylinder filled with palladium pellets* for conversion of traces of oxygen to water.

* A commercial unit supplied by Engelhard Ind., Inc., N. J.

The gas was then passed through an Ascarite tower to remove water vapor and carbon dioxide. The gas entrance tube into the cell was arranged so that the gas impinged directly on the palladium foil so that a fresh supply of purified hydrogen continually swept the electrode surface (ref. 12).

The electrode was first saturated with hydrogen by purging the fuel compartment with the gas until the electrode potential became constant for at least 10 minutes. The right hand side of the foil (Figure 9) was then anodically polarized by a potentiostat* for one minute each in potential increments of 100 mv until either a current density of 250 ma/cm² or the oxygen gassing potential was attained.

The palladium-silver foil was heat treated in air for one hour at 600°C before plating with rhodium black. Rhodium was plated first for 15 minutes at 10 ma/cm² and then for 35 minutes at 40 ma/cm² in a 0.005M solution of rhodium chloride adjusted to pH 1 with hydrochloric acid. All tests were made at room temperature. However, the temperature of the electrolyte increased slowly during the tests. Results are plotted as log I vs E by adjusting IR drop between the Pd-Ag electrode and a Luggin capillary until a straight Tafel relation was obtained for a range of current densities. Potentials at various current densities on the adjusted curve are given in Table 3.

a. Effect of Rhodium Plating On Oxidized Foil

Rhodium plating on oxidized foil with no further treatment was deleterious to the anodic polarization characteristics as shown by a comparison of Tests 1 and 2, Table 3. The oxide film formed by preliminary heat treatment at 600°C, which was previously shown to be required for good anodic properties, was probably reduced by evolved hydrogen during the rhodium plating in the low pH solution.

*Wenking (West Germany) Model 6376TR

Table 3

EFFECT OF RHODIUM PLATING ON ANODIC POLARIZATION OF PALLADIUM-25% SILVER DIFFUSION ELECTRODES

Electrode Potential vs HE at Same pH and Temperature (volts)

Electrolyte: 5M KOH; Fuel: Hydrogen Gas; Temperature: Room Temperature

Test No.	Electrode Preparation	Current Density ma/cm ²										Remarks
		0	8	16	32	80	160	240	320	400		
1	1 hr in air at 600°C	0.00	0.30	0.40	0.47	0.58	0.65	0.70	0.73	-	Max. Current Density 55 ma/cm ² at 0.29 v vs HE	
2	1 hr in air at 600°C Rh plating on elect. side	0.00	-	0.11	0.19	-	-	-	-	-		
3a	1 hr in air at 600°C Rh plating on elect. side 1 hr in air at 650°C	0.03	0.11	0.12	0.16	0.29	0.41	0.49	0.54	0.63	Electrolysis continued at 400 ma/cm ² . Best potential of 0.48 volt attained as temperature gradually increased. Current diminished to almost zero overnight.	
3b	(duplicate runs)	0.00	0.01	0.11	0.15	0.26	0.37	0.44	0.49	0.58		
4	1 hr in air at 600°C Rh plating on fuel side 1 hr in air at 650°C	0.00	0.31	0.39	0.48	0.59	-	-	-	-	Limiting current density, 120 ma/cm ² , reached at 0.64 volt	
5	1 hr in air at 600°C Rh plating on both sides 1 hr in air at 650°C	0.00	0.11	0.12	0.16	0.30	0.42	0.49	0.55	0.63	Electrolysis continued at 400 ma/cm ² . Max. potential was 0.57 volt. Current started to drop after 10 hours.	
6	3 hr in H ₂ at 600°C	0.11	-	-	-	-	-	-	-	-	No current was drawn until the potential reached that of oxygen evolution.	
7	1 hr in air at 600°C 3 hr in H ₂ at 600°C	0.08	0.58	-	-	-	-	-	-	-	Max. current density 14 ma/cm ² , reached at 0.72 volt.	
8	1 hr in air at 600°C 3 hr in H ₂ at 600°C Rh plating on electrolyte side	0.05	0.25	0.50	-	-	-	-	-	-	Max. current density 19 ma/cm ² , reached at 0.62 volt.	
9	1 hr in air at 600°C 3 hr in H ₂ at 600°C Rh plating on electrolyte side 1 hr in air at 650°C	0.08	0.34	0.40	0.46	0.55	0.61	0.65	0.70	-	Limiting current density 330 ma/cm ² at 0.70 volt.	

b. Effect of Oxidizing after Rhodium Plating

Good current density relations (0.38 volt polarization at 100 ma/cm²) were obtained by polarizing foils that had been rhodium plated and then oxidized at 650°C (Test 3a and 3b). Much better results were obtained than those for the control electrode (Test 1) which was oxidized only without plating. Duplicate experiments, a and b for Test 3, were in good agreement.

PdO, then, is an effective catalyst for the oxidation of H₂ from the molecular to the ionic state, resulting in improvement of overall utilization of H₂ fuel. The addition of Rh improves the catalytic action of PdO. Mechanisms involved in the effect of Rh plating are assumed as follows:

Rhodium is oxidized in air at 650°C to form Rh₂O₃ and RhO.

The addition of Rh₂O₃ to PdO increases the concentration of cation vacancies and decreases the ratio of the concentration of electron deficits to the concentration of cation vacancies according to the following equation:



where Rh⁺⁺⁺(Pd) denotes Rh⁺⁺⁺ ions on Pd⁺⁺ vacant sites. The increase in the concentration of cation vacancies would then benefit the electrode performance.

c. Effect of Location of Rhodium Plating

Rhodium plating was effective only at the electrolyte surface and was ineffective at the gas surface, as is shown by a comparison of Tests 3 and 4 (Table 3). Electrode 3, plated on the electrolyte side only, had excellent anodic polarization characteristics, while electrode 4, plated on the gas side only, polarized severely at low current densities. A palladium-silver foil, plated with rhodium on both sides, showed the same good anodic behavior as foils plated on the electrolyte side only (Test 5).

6. Effect of Heat Treating in Hydrogen Atmosphere

All heat treatments of electrodes in hydrogen (with or without an initial oxidation in air) resulted in deactivating the electrode as an anode, as shown in Tests 6, 7, and 8, Table 3. These experiments are additional evidence that palladium oxide is a fundamental catalyst for hydrogen transfer and oxidation, and reduction of this oxide with hydrogen deactivated the electrode. When an electrode was heat treated in hydrogen and then oxidized in air at 650°C (Test 9) the anodic properties were greatly improved compared with Tests 6, 7, and 8, but the polarization curve was not as good as that of Tests 3 and 5 without high-temperature hydrogen treatment.

7. Duration of Palladium-Silver Foil Activation

The rhodium-plated palladium-silver foils of the type used in Tests 3 and 5 were polarized for 10 hours at constant potential before current failure occurred. The reduction of palladium oxide by hydrogen at room temperature, which is thermodynamically favorable, is probably the cause of the electrode degradation.

8. Conclusions

The following tentative conclusions have been made after examining the polarization data of heat-treated and rhodium-plated palladium-silver electrodes. This work is still in progress, so these conclusions will be subject to review in subsequent reports.

1. PdO is an effective catalyst for the oxidation of H₂ from the molecular to the ionic state, resulting in improvement of overall utilization of H₂ fuel. The addition of Rh improves the catalytic action of PdO.
2. Full annealing of the palladium-silver foil improved the electrode performance.
3. The oxide coating formed at 700°C after full annealing at 850°C resulted in the best anodic polarization for the palladium-silver electrode, particularly at high current densities.
4. Thick oxide films formed by temperature cycling did not improve electrode characteristics. Polarization was actually more severe at high current densities for the thick oxide electrodes.
5. Rhodium plating on the electrolyte side of the palladium-silver foil improved the electrode performance only if the foil was oxidized after plating.
6. Heat treating foils in a hydrogen atmosphere degraded the electrodes by reducing the palladium oxide catalytic film.

C. PROGRAM FOR THE SECOND QUARTER

1. Determine the effect of addition of metals other than rhodium to the PdO film to further improve electrode performance and to establish the electrode mechanism.
 - (a) High valency metals - Ti, Zr, Th, Sn, Al, Fe, Cr, Ru, Ir.
 - (b) Low valency metals - Ag, Cu, Li.
 - (c) Bivalency metals - Ni, Co, Mg, Pt.
 - (d) Metals to form an oxide of n-type semiconductor - Mg(MgO), Th, (ThO₂), Ti(TiO₂), Zr(ZrO₂), Fe(Fe₂O₃), Al(Al₂O₃), Sn(SnO₂).
 - (e) Metals to form an oxide of p-type semiconductor - Cr(Cr₂O₃), Fe(FeO), Ni(NiO), Co(CoO), Cu(Cu₂O), Ag(Ag₂O).
 - (f) Metals to form an oxide of amphoteric type semiconductors - Cr(Cr₂O₃), Ir(IrO₂), Ru(RuO₂), Ti(TiO, Ti₂O₃).
2. Determine the effect of alloy grain size on electrode characteristics.
3. Determine the effect of traces of impurities on palladium-silver electrode performance by using a 99.99% pure alloy.

IV. ELECTRODES AND FUEL CELLS IN AQUEOUS SYSTEMS

A. ANODIC OXIDATION OF HYDRAZINE AT SOLID PALLADIUM DIFFUSION ELECTRODE

The solid palladium membrane was tested for anodically oxidizing 85% hydrazine hydrate in 5M sulfuric acid electrolyte. The cell arrangement is shown in Figure 10. The 0.001-inch palladium membrane was cleaned by boiling it in concentrated potassium hydroxide, rinsing it with distilled water, and quickly dipping in concentrated hydrochloric acid. The membrane was mounted in the test cell and then plated in 0.005M RhCl_3 for grey coatings and in 0.05M RhCl_3 for shiny coatings. Plating solutions were de-aerated by purging with helium. The 2.5 cm^2 membrane was plated at 2 ma for 30 minutes.

Results of tests with three different palladium membranes are shown in Table 4. The two membranes with grey rhodium coatings showed reasonable reproducibility, and both performed better at very high current density than palladium foils with shiny rhodium coatings. Tests at 30, 60, and 90°C were made for each membrane. Tests at each temperature required between 15 and 20 minutes to run. The half cell ran a total of one hour for all tests.

B. ANODIC OXIDATION OF HYDRAZINE AT POROUS TEFLON DIFFUSION ELECTRODE

An important candidate for a fuel-cell system is hydrazine with either nitric acid or dinitrogen tetroxide as the oxidant. The palladium membrane has been shown to be attacked at elevated temperatures by a trace of nitric acid. Unless palladium membranes can be alloyed with platinum for greater resistance to nitric acid (ref. 13), palladium foil cannot be used as a hydrazine electrode with nitric acid or dinitrogen tetroxide as the oxidant. Therefore, the "porous Teflon vapor diffusion electrode" (PTVDE) offers the best possibility of utilizing hydrazine with nitric acid.

One scheme for using the PTVDE electrode is to feed 85% hydrazine hydrate to the back of the electrode and allow hydrazine vapor to pass through the electrode to the actively catalyzed side. Another proposal is to decompose the hydrazine to nitrogen and hydrogen gases, which are then fed to the porous Teflon electrode. The latter scheme has the advantage of not contaminating the electrolyte with hydrazine or, if sulfuric acid is the electrolyte, of not forming a precipitate of hydrazine sulfate at the anode surface.

The system used for decomposing the hydrazine and feeding nitrogen and hydrogen gas to the PTVDE is shown in Figure 11. Rhodium black

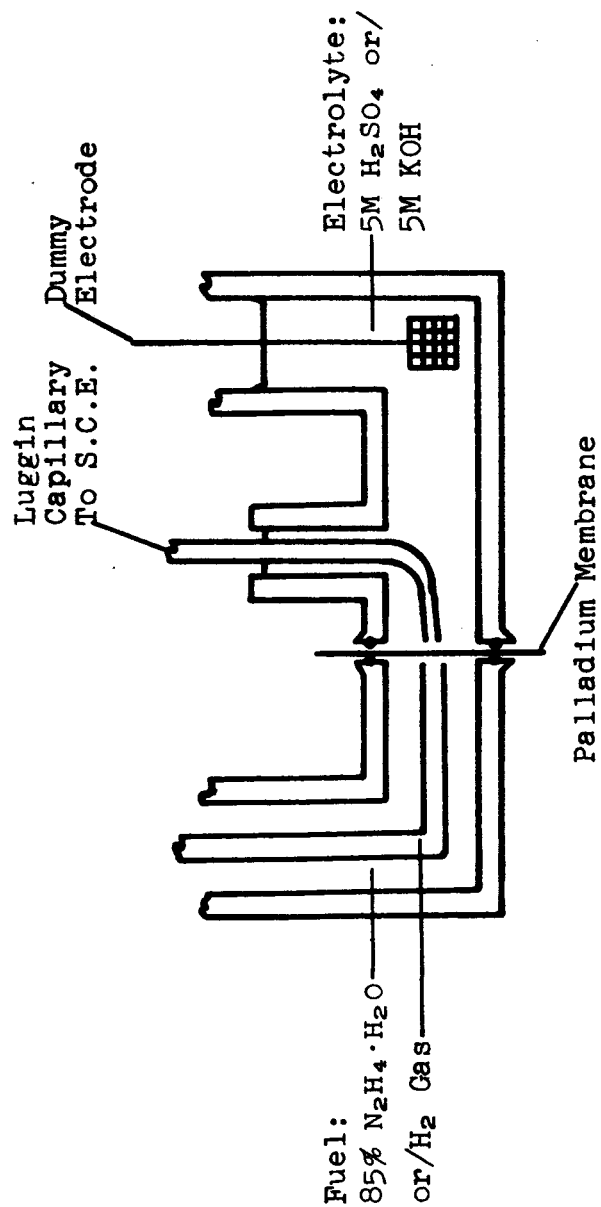


Figure 10. Half Cell Construction for Testing
Palladium Membrane Electrodes

Table 4

ANODIC POLARIZATION OF PALLADIUM MEMBRANE ELECTRODE UTILIZING 85% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ AS HYDROGEN SOURCEElectrolyte - 5M H_2SO_4 ; Anode - Pure 0.001-inch Palladium

*Voltage vs HE at Same Temperature and pH

Current Density $\frac{\text{ma}}{\text{cm}^2}$	Grey Coating No. 1			Grey Coating No. 2			Shiny Coatings		
	30°C	60°C	90°C	30°C	60°C	90°C	30°C	60°C	90°C
O(O.C.V.)	0.05	0.04	0.04	0.04	0.03	0.03	0.03	0.02	0.01
20	0.07	0.05	0.04	0.08	0.06	0.03	0.07	0.04	0.03
40	0.11	0.06	0.05	0.14	0.07	0.07	0.24	0.09	0.03
120	----- **	0.07	0.05	-----	0.10	0.08	-----	-----	0.06
200	-----	0.10	0.06	-----	0.30	0.09	-----	-----	0.13
280	-----	0.14	0.08	-----	-----	0.12	-----	-----	-----

* All Voltage Measured with Kordes-Marko bridge.

** All dashed lines indicate that electrode potential passed into the oxygen evolution region before reaching listed current density.

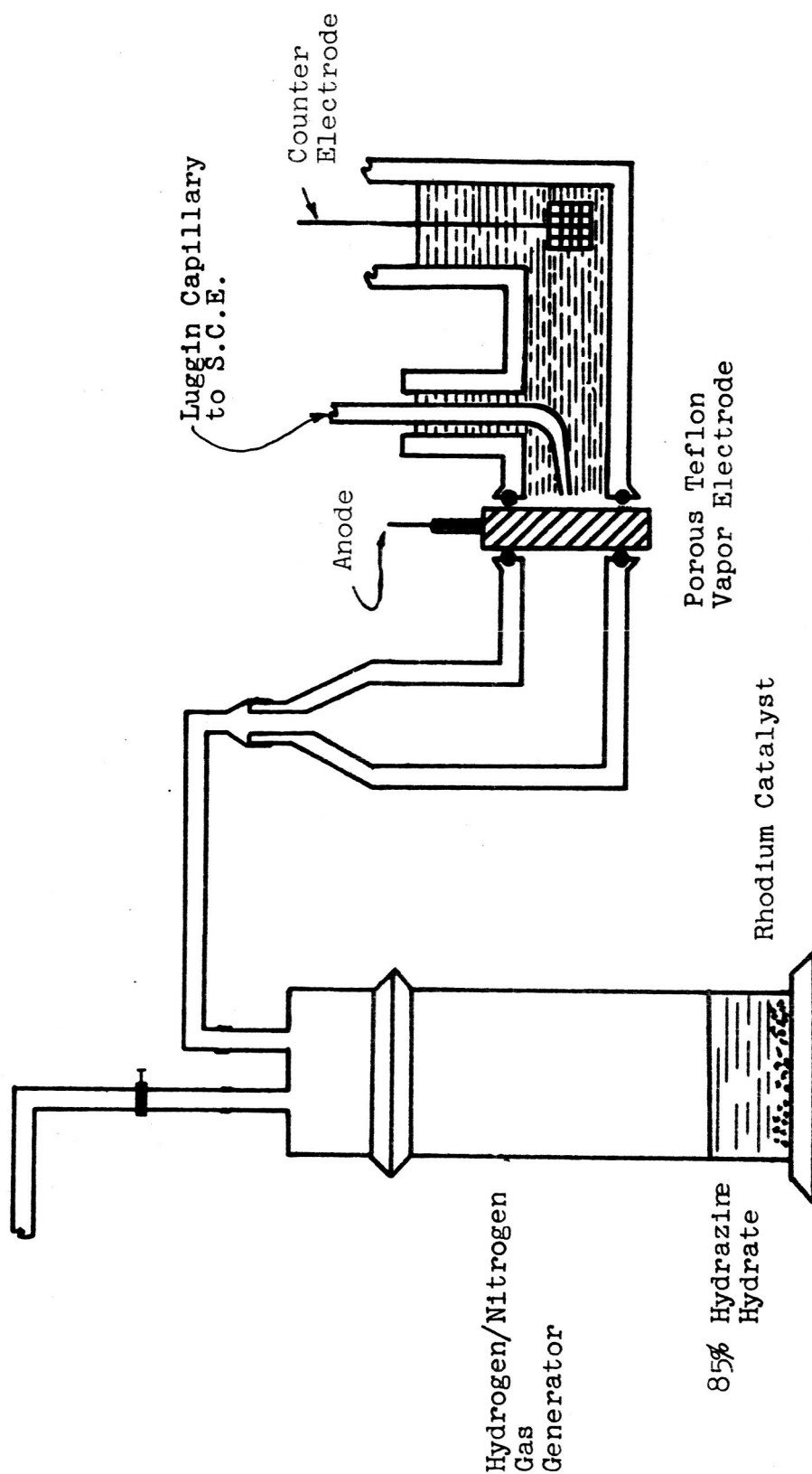


Figure 11. Apparatus for Externally Decomposing Hydrazine to Hydrogen and Nitrogen and Using the Product Gas at Porous Teflon Anode.

powder* was used to decompose 85% hydrazine hydrate in an external flask. The rate of hydrogen production was sufficient to support a current of 300 ma/cm², based on the reaction $\text{N}_2\text{H}_4 \longrightarrow \text{N}_2 + 2\text{H}_2$. Results of two hydrazine decomposition tests are given in Table 5. Rates of gas formation were measured for the second run. Steady currents of 200 ma/cm² could be maintained. At currents higher than 250 ma/cm², the potentials slowly deteriorated.

Details of the preparation of the PTVDE were given in the last final report (ref. 14). A catalyst loading of 50 mg/cm² of platinum powder* was pressed into a double thickness Teflon-impregnated glass membrane**. The experimental current efficiency of 70% may be less than theoretical because of insufficient active catalyst surface, or nonhomogenous catalyst area, allowing hydrogen to penetrate without contacting catalyst.

The hydrazine-nitric acid cell made with porous Teflon electrodes should have a good voltage and low polarization. However, the nitrogen by-product of hydrazine decomposition must be fed through the PTVDE and may cause difficulties in the full cell design. Alternately, a conventional gas electrode with circulating gas might be used.

C. SELECTIVITY OF CARBON AND PLATINUM AS CATALYSTS FOR NITRIC ACID AND HYDRAZINE

We have previously reported that carbon is selective to the reduction of nitric acid, even in the presence of 0.5M hydrazine (ref. 14). Through an oversight, the data were not given in the final report. Table 6 contains these data combined with those for platinum and ruthenium-catalyzed carbons in the same solutions.

The data show that even with 0.5M hydrazine and 5M nitric acid, FC-13 carbon[†] acts as a specific catalyst for nitric acid at either 30°C or 90°C. FC-14 carbon[†] is less active but is still specific. The platinum-catalyzed FC-14 carbon functions as a fair anode (is hydrazine selective) with 0.3M hydrazine in 5M nitric acid at 90°C. Ruthenium-catalyzed FC-14 carbon shows a mixed potential and is not selective to either reactant.

*Englehard Industries, Inc., Newark, N. J.

**Pall TV-20-30A

†Pure Carbon Company, Inc., St. Marys, Pennsylvania

Table 5

EXTERNAL HYDRAZINE DECOMPOSITION AND UTILIZATION AT POROUS TEFLON ELECTRODE

Electrolyte - 5M H₂SO₄; Anode - PTVDE, 50 mg Pt/cm², Temperature - 30°C

Current Density ma/cm ²	<u>Potential vs HE at same Temperature and pH</u>	
	<u>Test I</u>	<u>Test II</u>
0	0.060	0.060
4	0.060	0.075
8	0.060	0.075
20	0.065	0.075
40	0.070	0.080
60	0.070	0.09
80	0.080	0.10
100	0.085	0.11
120	0.09	0.12
200	-----	0.16

Note: For Test II H₂ production rate our feed rate measured assuming N₂H₄ → N₂ + 2H₂

Total gas evolution rate at 30°C = 9.0 cc/min

H₂ rate = 4.3x 10⁻⁶ moles/sec

Maximum current for H₂ rate = 330 ma/cm²

Table 6

ANODE AND CATHODE POLARIZATION TESTS
SHOWING SELECTIVITY OF CATALYSTS TOWARD
COMPONENTS OF N_2H_4 - HNO_3 SOLUTIONS

Reactants		Current Density ma/cm ²	Potential vs SHE*						Notes	
			Electrode Material							
<u>N₂H₄</u>	<u>HNO₃</u>		<u>FC-13</u> 30°C	<u>FC-14</u> 30°C	<u>FC-14</u> 90°C	<u>Pt on FC-14</u> 30°C	<u>Pt on FC-14</u> 90°C	<u>Ru on FC-14</u> 30°C		<u>Ru on FC-14</u> 90°C
None	5M	0	1.14	1.13	1.10	1.11	1.12	1.12	All tests run as cathode	
		10	1.10	1.11	1.08	1.08	1.07	1.07		
		20	1.09	1.10	1.07	1.07	1.06	1.06		
		50	1.07	1.09	1.05	1.05	1.05	1.05		
0.1M	5M	100	1.05	1.07	1.02	1.03	1.03	1.04	Pt on FC-14 tested as anode	
		0	1.12	1.14	1.06	0.42	1.06	1.06		
		10	1.10	1.13	1.04	---	1.05	1.05		
		20	1.09	1.12	1.03	---	1.04	1.04		
0.3M	5M	50	1.07	1.11	1.02	---	1.03	1.03	Ru on FC-14 would not function as anode or cathode. Pt on FC-14 tested as anode	
		100	1.06	1.10	1.00	---	---	---		
		0	---	---	1.03	0.34	0.32	0.68		0.67
		10	---	---	1.02	0.53	0.36	---		---
0.5	5M	20	---	---	1.01	---	0.43	---		
		50	---	---	0.98	---	0.49	---		---
		100	---	---	0.95	---	0.59	---		---
		0	1.11	1.10	1.07	1.07	1.04	---		---
		10	1.09	1.10	1.02	1.07	---	---		
		20	1.08	1.10	1.01	---	---	---		---
		50	1.06	1.09	---	---	---	---		---
		100	1.03	1.08	---	---	---	---		---

*SHE = Standard Hydrogen Electrode ($a_{H^+} = 1$) (SCE = 0.24 volt) This reference was used since the exact value of HE (hydrogen electrode at same temperature and pH) cannot be calculated, but should be close to SHE.

From the data shown, if an FC-13 cathode and platinized FC-14 anode were used in the same fuel-oxidant-electrolyte solution (0.5M N_2H_4 - 5M HNO_3), an open-circuit potential of about 0.8 volt at 90°C should result. At 50 ma/cm², the voltage should be at least 0.60 volt, while at 100 ma/cm² a voltage of 0.5 volt could be obtained.

D. FULL-CELL CONSTRUCTION AND TESTING

1. Hydrogen Peroxide-Hydrogen Cell

A complete cell using a PTVDE cathode with hydrogen peroxide and a rhodium-catalyzed palladium anode with 85% hydrazine hydrate is shown in Figure 12. The electrolyte compartment was made by combining three silicon rubber gaskets with a gas vent in the middle. The separation between electrodes was about 3 mm. The electrolyte was 5M potassium hydroxide. Data for two such cells are listed in Table 7. The cell resistance in ohm-cm² was determined by dividing the IR drop across the cell by the current density. The IR drop was taken as the difference between the cell voltage and the Kordes-Marko bridge voltage (IR-free). The cell resistance values of 2 to 3 ohm-cm² are larger than the calculated resistance for 3 mm of 5M potassium hydroxide at 30 and 50°C (0.4 ohm-cm² and 0.3 ohm-cm², respectively),** so our measured values may include contact resistances.

The best cell output, 0.70 volt at 40 ma/cm² represents a promising start in full-cell development. Each cell ran for about three hours before severe deterioration. At the time of voltage failure, the peroxide concentration had dropped from 10M to about 2M in the bulk feed solution. Rejuvenation of the peroxide concentration improved the cell performance to close to the original conditions.

2. Oxygen-Hydrogen (or Hydrazine) Cell (3-in. by 3-in. Electrodes)

Work was started on the construction and testing of fuel cell units with an electrode area of 9 sq in. Hydrogen and hydrazine were tested as fuels, and oxygen and hydrogen peroxide were tested as oxidants.

Construction details for the fuel cell are shown in Figure 13. The end plates were made of nickel plated stainless steel. The corrugated structure of the end plate allows uniform reactant distribution while making good electrical contact with the conducting electrode surface. The anode consisted of a solid palladium hydrogen diffusion membrane, 0.001 in. thick, supported on the back side by 0.030 in. thick nickel plaque.* The nickel plaque had a porosity of approximately 75% and so did not seriously affect the ease of fuel transport to the back side of the palladium anode. Both sides of the

* Gould National Batteries, Inc., St. Paul, Minnesota.

** Lange's Handbook of Chemistry; Calculated from data listed at 15°C using a 2% per degree temperature correction.

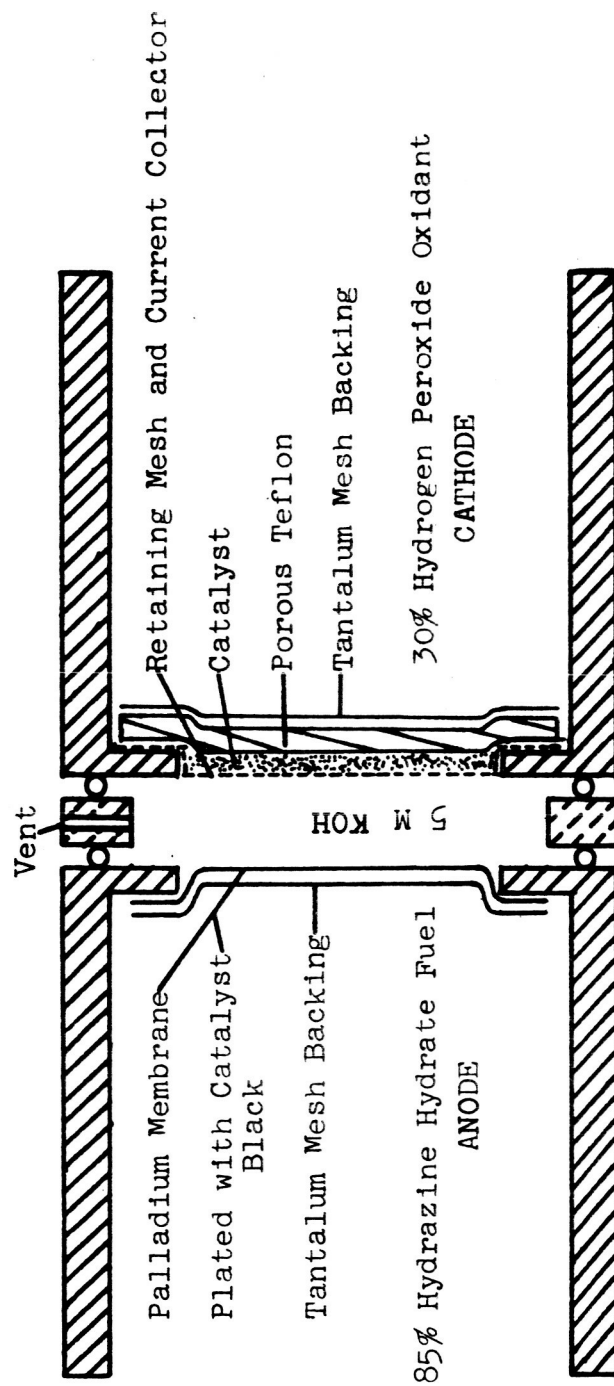


Figure 12. Complete Hydrogen Peroxide-Hydrazine Cell

Table 7

HYDRAZINE - HYDROGEN PEROXIDE FULL CELL PERFORMANCE

Fuel: 85% Hydrazine Hydrate
 Anode: Palladium Membrane
 Cathode: PTVDE, 50 mg Pt/cm²
 Oxidant: 30% H₂O₂
 Temperature: 35°C - 50°C
 Electrolyte: 5M KOH

Current Density ma/cm ²	Cell I				Cell II			
	<u>V_{k-m}</u>	<u>V_{IR}</u>	<u>IR drop</u>	<u>Resistance ohms-cm²</u>	<u>V_{k-m}</u>	<u>V_{IR}</u>	<u>IR drop</u>	<u>Resistance ohms-cm²</u>
0	---	0.99	---	-----	----	1.00	----	-----
2	0.93	0.91	0.02		0.975	0.96	0.015	7.5
4	0.92	0.91	0.01		0.96	0.945	0.015	3.75
8	0.89	0.865	0.025	3.1	0.92	0.89	0.030	3.75
12	0.88	0.85	0.03	2.5	0.915	0.89	0.025	2.1
20	0.85	0.81	0.04	2.0	0.875	0.845	0.03	1.5
30	0.73	0.67	0.06	2.0	0.76	No longer using KM Bridge, but loading external resistor.		
40					0.70			
100(max current)					0.15			

V_{k-m} is IR free voltage measured on Kordesch-Marko bridge.
 V_{IR} is voltage, including IR component, measured directly.

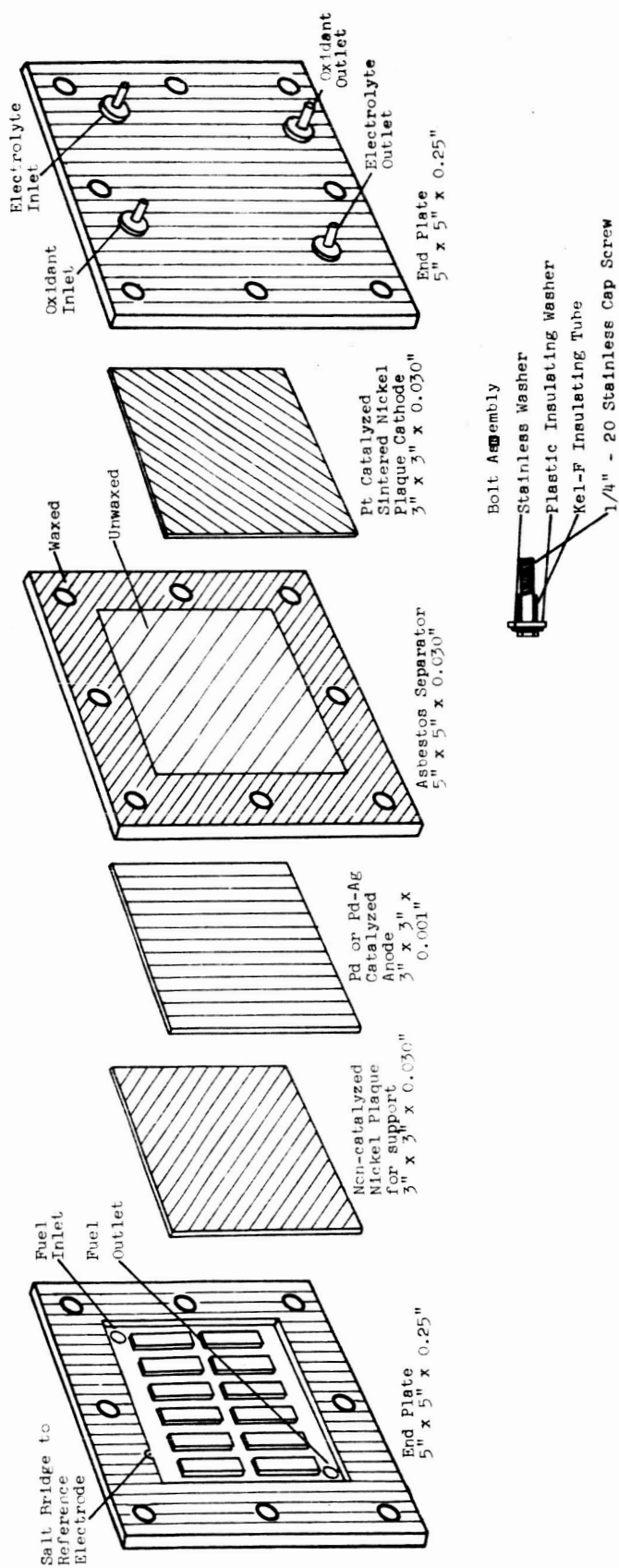


Figure 13. Exploded View of Full Cell

palladium foil were catalyzed with rhodium by electroplating from a 1% rhodium chloride (RhCl_3) solution, adjusted to pH 1 by adding hydrochloric acid. A black coating of rhodium was deposited on the 3 inch by 3 inch foil by passing a current of 200 to 500 ma between a 1 cm^2 platinum anode and the surface of the palladium foil. The anode was moved manually to different positions close to the foil until the surface was completely darkened. After plating, the palladium was heat treated at 700°C for 1 hour. The palladium foil was reactivated after use by heat treating at 700°C for 2 to 4 hours.

The cathode was made from the same nickel plaque, catalyzed with either platinum or platinum-palladium. Both metals were spontaneously chemiplated on the porous nickel surface from dilute chloride salt solutions. A precious metal loading of 25 mg/sq in. was used.

The electrolyte, 5M potassium hydroxide, saturated a 0.030-inch thick asbestos mat which also served to electrically insulate the anode from the cathode. The outside edges of the asbestos mat were sealed with a 100°C melting point wax. The back of one end plate was drilled and fitted with Teflon tubing stuffed with highly compressed asbestos as a Luggin capillary between the back side of the porous electrode and a reference electrode outside of the fuel cell. This reference electrode was used to determine which electrode was polarized after voltage failure during discharge.

Results of initial experiments with the palladium membrane fuel cell using oxygen as the oxidizer and hydrogen or hydrazine as the fuel are given in Table 8. The best power output for the cell was 2.1 watts or 37 mw/cm^2 at 90°C with oxygen and hydrazine. At the end of the test, half-cell measurements showed that the cathode only was appreciably polarized.

An alternate method of preparing the palladium membrane consisted of first heat treating the foil and then electroplating with rhodium. Palladium membranes prepared in this manner were not as good anodes as those made by first plating and then heat treating.

Hydrogen peroxide could be used as an oxidant for only short periods because of the rapid evolution of oxygen when heated in contact with the catalyzed electrodes. For a five minute period, 105 ma/cm^2 was drawn at 0.40 volts. Hydrogen peroxide thus offers a good possibility as an oxidant if spontaneous oxygen release can be controlled.

Table 8
OXYGEN AND HYDROGEN (OR HYDRAZINE) FULL CELL*
Electrolyte - 5M KOH

Temp. °C	Fuel	Current Density ma/cm ²	Voltage IR-free volts	Cell Voltage IR-included volts	R ohms-cm ²	Cumulative Time hr	Notes
67	H ₂	0	--	1.02	--	0	
68	"	1	0.965	0.965			
68	"	1.7	0.965	0.945		0.25	
69	"	3.4	0.92	0.91	2.9		
69	"	6.8	0.865	0.84	3.9	0.50	
70	"	12.1	0.78	0.74	3.3		
73	"	16.6	0.62	0.55	4.2	0.75	P _{O2} = 10 psig P _{H2} = 10 psig
74	"	16.6	0.65	0.60	3.0	1.0	Purging H ₂ increased output
78	"	16.6	0.78	0.76	1.2	2.0	
83	"	29.6	--	0.60		2.5	Slow H ₂ Purge
84	"	36.2	--	0.45		3.0	
80	100% N ₂ H ₄ ·H ₂ O	16.6	--	0.78		5.0	
90	"	55	--	0.60		6.0	
90	H ₂	43	--	0.50		8.0	Purging H ₂
90	"	52	--	0.60		9.5	
30	100% N ₂ H ₄ ·H ₂ O	0	--	0.99			
30	"	16.8	0.50	0.38	6.9	10.5	
90	"	57	--	0.65	--	13.0	Cathode** Limiting Cell

*Anode Pd-Ag membrane 3 x 3 x 0.001 inches
Rh plated and heat treated at 600°C

Cathode Ni plaque (Gould) 3 x 3 x 0.030 inches
Pt deposited (25 mg/sq. in.)

Separator Iron-Free Asbestos 0.030 inch thick

**Anode potential was 0.08 vs HE at same pH and Temperature
Cathode potential was 0.71 vs HE at same pH and temperature

E. PROGRAM FOR THE SECOND QUARTER

1. Investigate the construction variables for porous Teflon electrodes for use as cathodes for HNO_3 and N_2O_4 reduction.
2. Study the catalytic effect of different carbons and graphites for HNO_3 and N_2O_4 reduction.
3. Construct and demonstrate complete fuel cells using storable propellants as fuels and oxidant.

V. ANHYDROUS HYDROGEN FLUORIDE SYSTEMS

A. SOLID PALLADIUM-HYDRAZINE DIFFUSION ELECTRODE

The use of solid palladium for purification of hydrogen and as a hydrogen diffusion anode is well known (refs. 1, 2, 3, 4, 5, 6). Previous work at this Laboratory has shown that aqueous hydrazine can be used to charge a palladium membrane with hydrogen, and the hydrogen can be burned anodically on the opposite side of the membrane after diffusion through the foil. This scheme is attractive for the anhydrous hydrogen fluoride system, since the hydrazine reductant will be restricted from the electrolyte compartment and cannot come into contact with potent oxidizers such as chlorine trifluoride.

Also, the hydrazine may be used either in the anhydrous form or in aqueous solution, since water cannot pass through the palladium membrane to contaminate the anhydrous electrolyte.

A disk of 0.001-inch thick palladium*, 1 inch in diameter, was plated at 14 ma for 2 minutes for each side in a "Rhodex" proprietary rhodium plating solution.

The rhodinized palladium was mounted in a Teflon holder (Figure 14) which exposed a disk 0.5 inch in diameter (1.27 cm^2). A lead-lead fluoride reference electrode was placed adjacent to the electrode holder in one side of a Teflon "H" cell, and a lead counter electrode was mounted in the opposite side of the "H" cell. The Teflon electrode holder was filled with a solution of 5M hydrazine in 5M potassium hydroxide and the "H" cell filled with molten $\text{KF} \cdot 3\text{HF}$. The "H" cell was immersed in a fluidized sand thermostat for temperature control at 85°C . The open-circuit potential of the palladium membrane was measured, and the electrode was anodically polarized at successively increasing currents until drastic potential failure occurred. Potentials against the lead-lead fluoride reference were measured at the end of each 2-minute polarization period with both an electrometer and a Kordes-Marko bridge. The latter instrument measured polarized electrode potentials without IR drop. Results are tabulated in Table 9. The open-circuit potential was 0.05 volt more positive than that

*Englehard Industries Inc., Newark, N. J., 75% Pd, 25% Ag

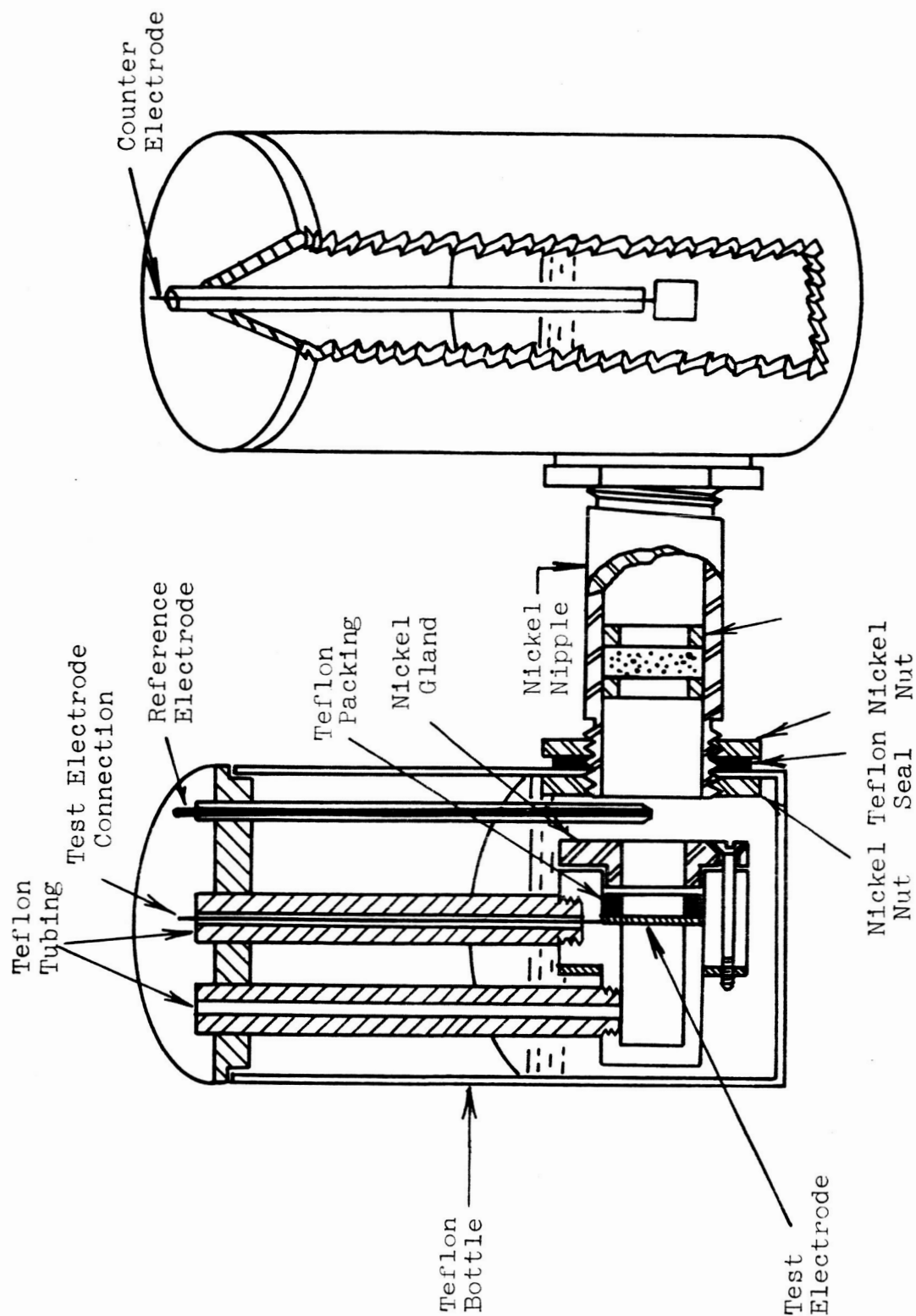


Figure 14. Polarization Cell for Hydrogen Fluoride Systems

Table 9

ANODIC POLARIZATION OF PALLADIUM-HYDRAZINE
ELECTRODE IN $\text{KF} \cdot 3\text{HF}$ AT 85°C

Fuel - $5\text{M N}_2\text{H}_4$ in 5M KOH

<u>Current Density ma/cm²</u>	<u>Potential vs Hydrogen Electrode After 2 Minutes Polarization, volts*</u>
0	0.05
0.8	0.08
1.6	0.08
3.9	0.10
8.0	0.13
16	0.14
39	0.34

*IR-free

of the hydrogen electrode in the same electrolyte. The electrode withstood a current density of 39 ma/cm² before severe polarization occurred. This experiment demonstrated that the palladium-hydrazine electrode can be used in anhydrous hydrogen fluoride systems. To avoid anodic attack of the palladium, the potential must be maintained at a potential less than 0.5 volt positive to the lead electrode (see next section). The normal potential of the electrode in contact with hydrazine is in a suitable region to avoid anodic attack. Further work will be done to improve the current-carrying characteristics of the palladium-hydrazine anode.

B. POROUS NICKEL-HYDROGEN ELECTRODE

A circular piece of porous nickel plaque*, 1 inch in diameter by 0.025 inch thick, was treated with 25 mg of platinum per square inch by spontaneous deposition from a dilute solution of chloroplatinic acid. The catalyzed disk was mounted in a Teflon holder which exposed 1.27 cm² of the electrode surface, as shown in Figure 14. The back side of the membrane was purged with hydrogen gas and the assembly immersed in KF·3HF at 85°C. A lead-lead fluoride reference electrode was placed adjacent to the electrode holder in one side of the Teflon "H" cell, and a lead counter electrode was placed in the opposite side of the cell. The free space in the assembly was purged with nitrogen gas. The electrode was anodically polarized as previously described for the palladium membrane.

The porous nickel-hydrogen anode withstood a current density of 39 ma/cm² before severely polarizing (see Table 10). The anodic polarization at this loading was more favorable than that of the palladium membrane at the same current density (Table 9). Future work will be directed toward improvement of the current-carrying ability of this electrode system.

C. REFERENCE ELECTRODES IN KF·3HF

Reference electrodes are required for both half-cell and full-cell studies in AHF solutions. Anodic and cathodic polarization curves for fuels or oxidants in AHF must be measured against a reference electrode that is compatible with the solvent and electrolyte. Aqueous reference electrodes, such as the calomel electrode, are not satisfactory for use with anhydrous systems because of contamination difficulties and because of the unknown liquid junction (ref. 15). The ideal reference electrode has a reproducible potential, is not readily polarized, returns quickly to its original open-circuit potential after polarization, and does not contaminate the working electrode or its electrolyte.

*Gould National Batteries, Inc., St. Paul, Minnesota

Table 10

ANODIC POLARIZATION OF HYDROGEN-POROUS NICKEL
ELECTRODE IN $\text{KF} \cdot 3\text{HF}$ AT 85°C

<u>Current Density ma/cm²</u>	<u>Potential vs Hydrogen Electrode After 2 Minutes Polarization, volts*</u>
0	0.00
0.8	0.00
1.6	0.00
3.9	0.01
8.0	0.03
16	0.08
39	0.20

*IR-free

The silver fluoride, copper fluoride, and lead fluoride electrodes have been suggested as reference electrodes in AHF solutions by Koerber and DeVries (ref. 16). These electrodes and the hydrogen electrode (platinized palladium) were tested in $\text{KF} \cdot 3\text{HF}$ solution at 85°C by anodic polarization at current densities as high as 100 ma/cm^2 . Details of the method of preparing these electrodes are given in the Appendix.

The anodic polarization of hydrogen, lead, silver, and copper electrodes in $\text{KF} \cdot 3\text{HF}$ at 85°C is shown in Figure 15. The silver, hydrogen, and lead electrodes withstood anodic currents up to 100 ma/cm^2 with little polarization, while the copper electrode was polarized 0.3 volt at this current density. The potential of the lead electrode is about 0.3 v more negative than the hydrogen electrode.

Although reduction to hydrogen would be expected at this potential, none was observed. Apparently lead has a high overvoltage for hydrogen reduction in $\text{KF} \cdot 3\text{HF}$ solutions. The very active potential of lead makes it a better reference candidate than the less active metals, since traces of lead ion would not be reduced at surfaces with a more positive potential and thus contaminate the test electrodes.

D. POTENTIOSTATIC ANODIC POLARIZATION MEASUREMENTS

Potentiostatic anodic polarization measurements have been shown to be a successful method for evaluating metal corrosion (refs. 8, 17). The degree of anodic protection present as a metal is subjected to gradually increasing anodic potentials is readily apparent by measuring the anodic current accompanying controlled polarization (refs. 18, 19).

1. Method

Solid metal specimens were prepared for anodic polarization measurements by polishing with 00 emery paper and washing in Triclene, water, and acetone. The total geometric surface area exposed to electrode was measured. The specimens were mounted in one side of a Teflon "H" cell with a lead-lead fluoride reference electrode close to the metal surface. A lead counter electrode was placed in the opposite side of the "H" cell. The cell was filled with molten $\text{KF} \cdot 3\text{HF}$, and the void space was purged with dry nitrogen gas. The assembly was placed in a fluidized sand bath thermostat maintained at 85°C . Polarization measurements were made with a potentiostat. After the open-circuit potential was measured, with reference to a lead reference electrode, the potential was fixed at successive intervals of 0.04 volt more positive than the open-circuit potential and the current recorded after one minute's polarization at each potential. These measurements were continued to a potential 1.8 volts

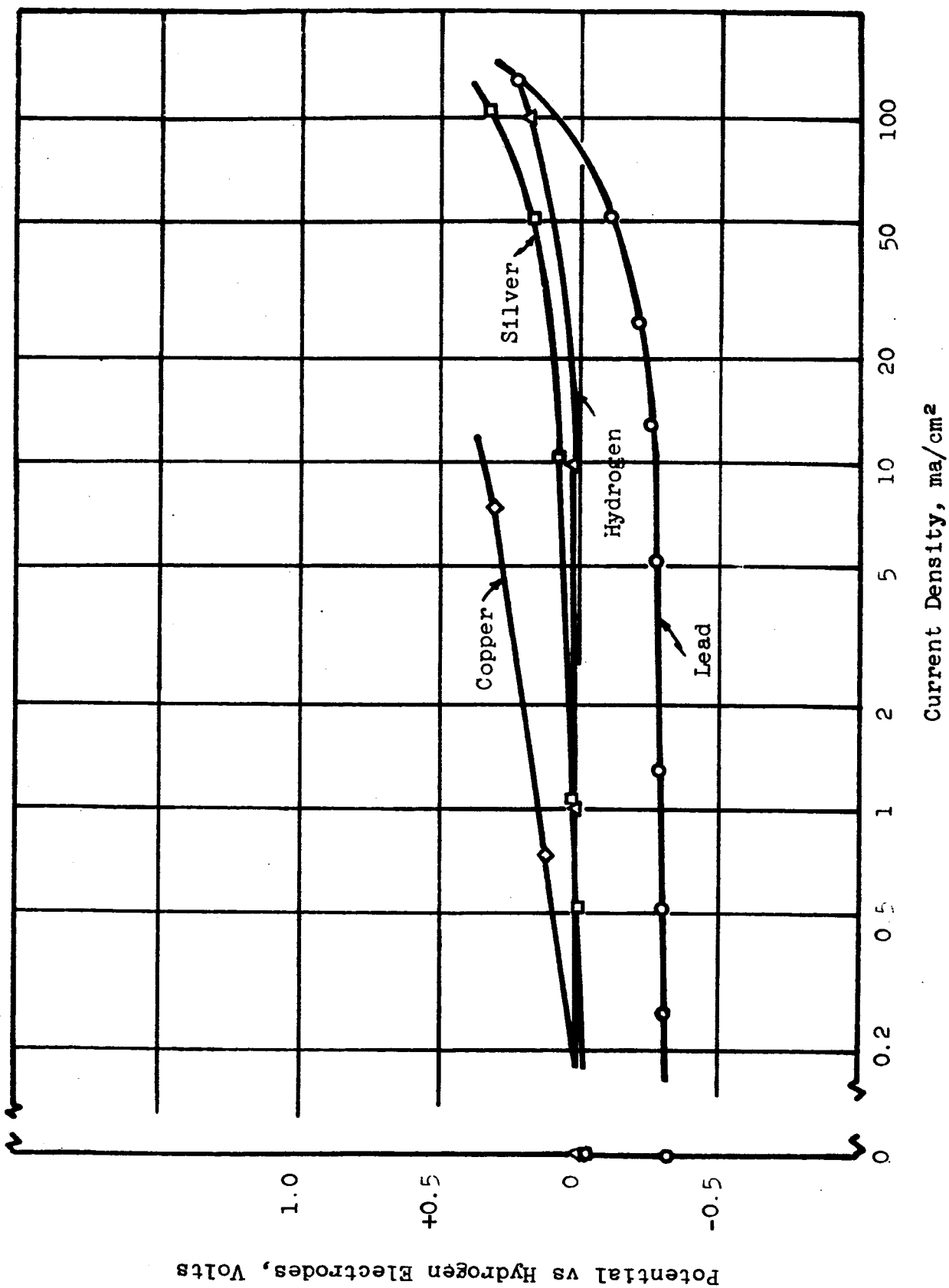


Figure 15. Anodic Oxidation of Hydrogen, Lead, Copper, and Silver in KF·3HF at 85°C

more positive than the lead reference, and the potential was adjusted in 0.04 volt negative intervals until the current changed from anodic to cathodic. The polarization pattern is shown in Figure 16 for solid nickel. The current increases steadily as the potential becomes more positive up to a potential 0.65 volt more positive than the reference electrode, after which the current reversed and was relatively constant at 15-25 μ a at potentials more positive than 0.8 volt. After reversing the polarization direction, a constant current region at 8-15 μ a occurred at potentials more positive than 0.8 volt, and a small current peak was recorded at 0.7 volt, after which the current fell to zero and became cathodic. The pronounced peaks and regions of small constant anodic currents are evidences of the formation of protective anode fluoride films on the nickel surface. Nickel is known to be a good construction material for fluoride and hydrogen because of its tendency to form tough protective anode films.

A specimen of porous nickel plaque was tested for corrosion in the KF \cdot 3HF melt by the same procedure as just described for solid nickel (see Figure 17). The anodic currents were many times higher for a given geometrical surface area than for the solid nickel specimen because of the much greater surface area of the sintered nickel and possibly a greater specific reactivity of the sintered metal. After the initial current peak at 0.7 volt to the reference electrode, the current decreased but not to the trivial values for the solid specimen as shown by Figure 16. The large anodic currents above 0.8 volt indicated appreciable attack instead of passivation. Additional tests with slower sweeping periods and longer potential spans will be required to further characterize the nickel plaque for use in the KF \cdot 3HF melt.

The anodic polarization of copper (Figure 18) resulted in much greater anodic currents than those incurred during solid nickel polarization (Figure 16). A maximum in the current-potential curve occurred at 0.8 volt positive to the lead-lead fluoride reference, but the current decreased only slightly at more positive potentials than 0.8 volt. Copper corrodes much more rapidly than nickel in the KF \cdot 3HF melt at 85°C and does not become readily passivated at high anodic potentials. Long-term tests would be required to more completely evaluate copper corrosion.

Anodic polarization of palladium (Figure 19) indicated that this metal is slowly anodically corroded in the KF \cdot 3HF melt at 85°C. Unlike nickel and copper, palladium did not show a maximum in the current-potential relation.

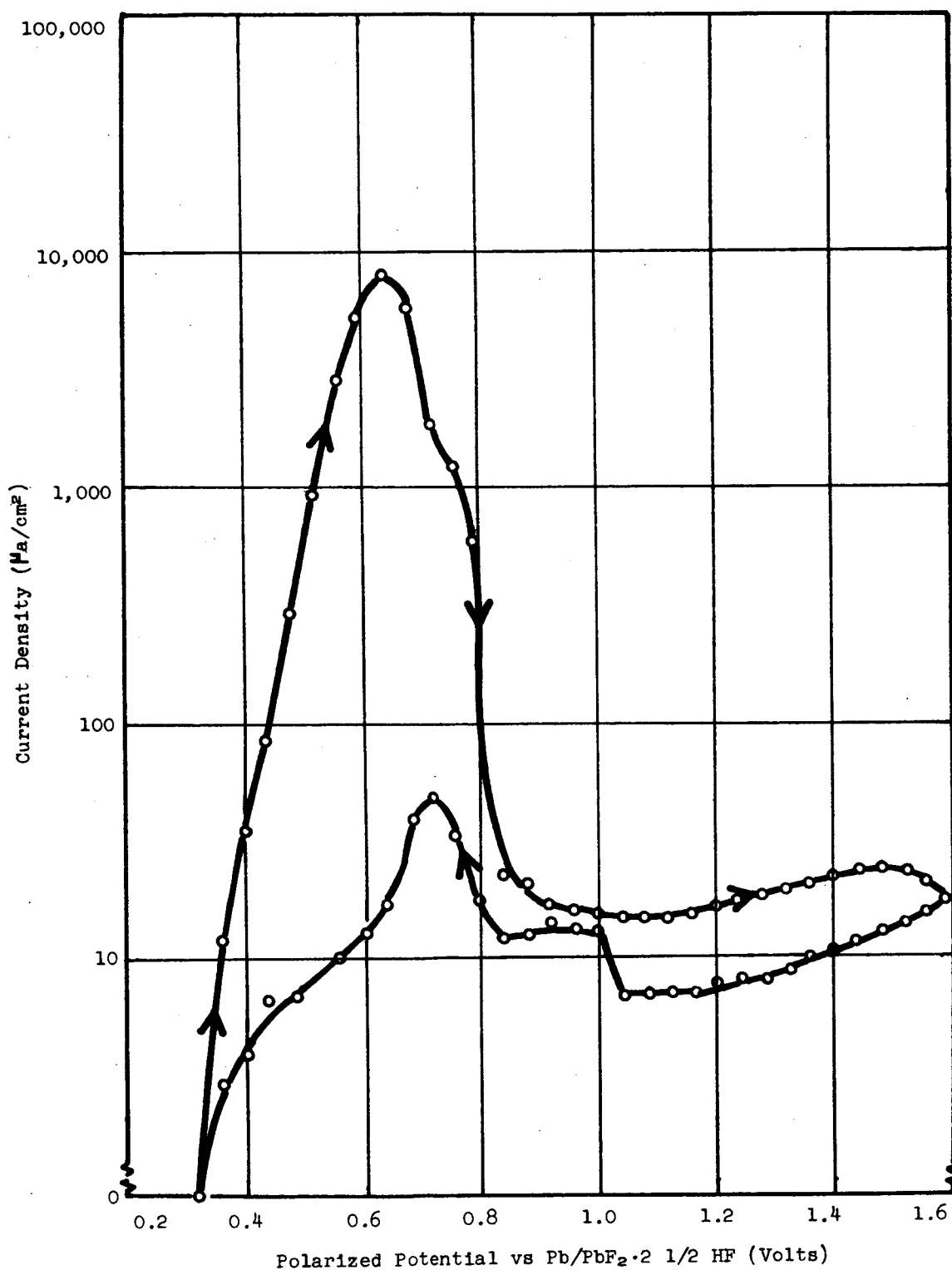


Figure 16. Potentiostatic Anodic Polarization of Solid Nickel in $KF \cdot 3HF$ at $85^\circ C$.

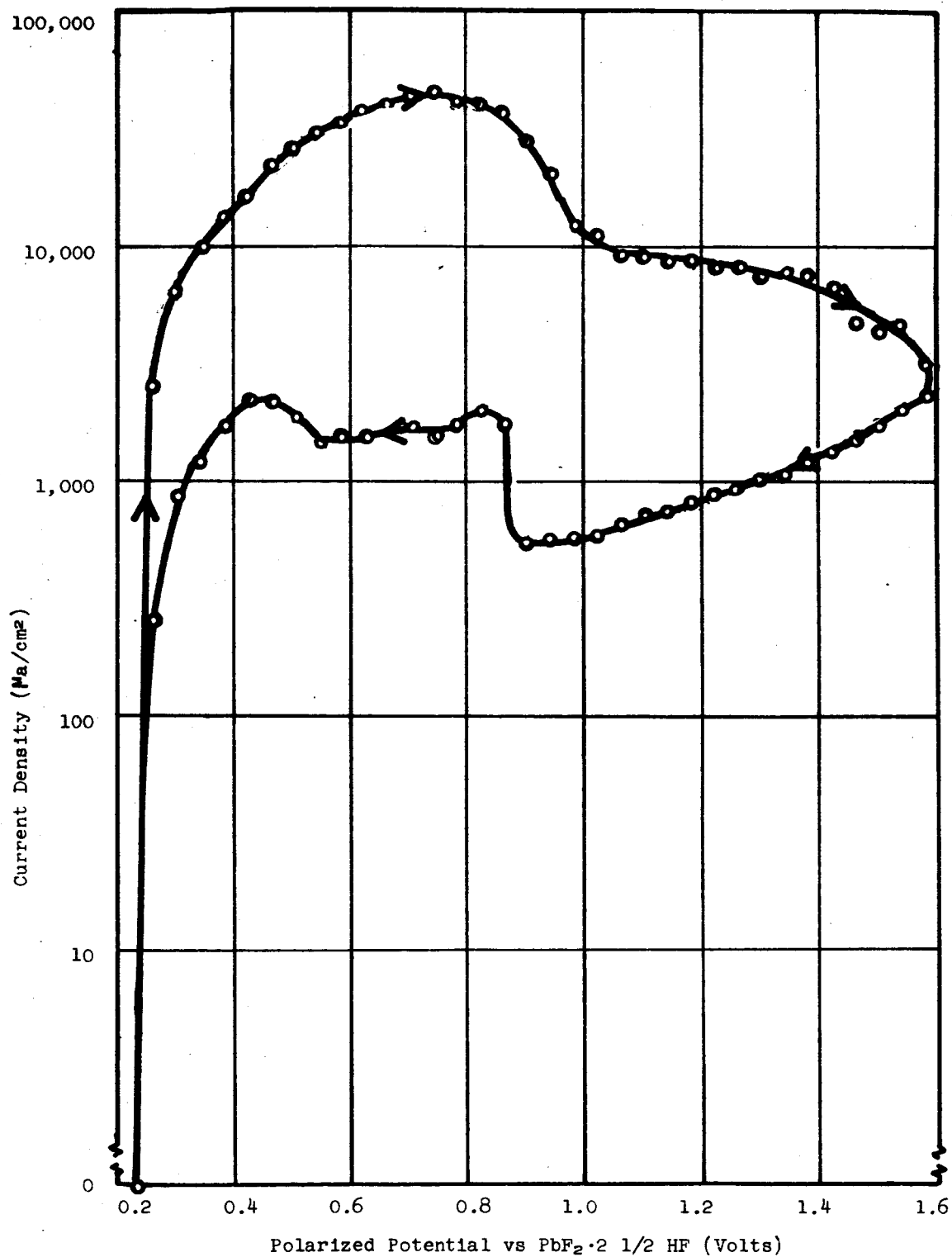


Figure 17. Potentiostatic Anodic Polarization of Nickel Plaque in $\text{KF} \cdot 3\text{HF}$ at 85°C .

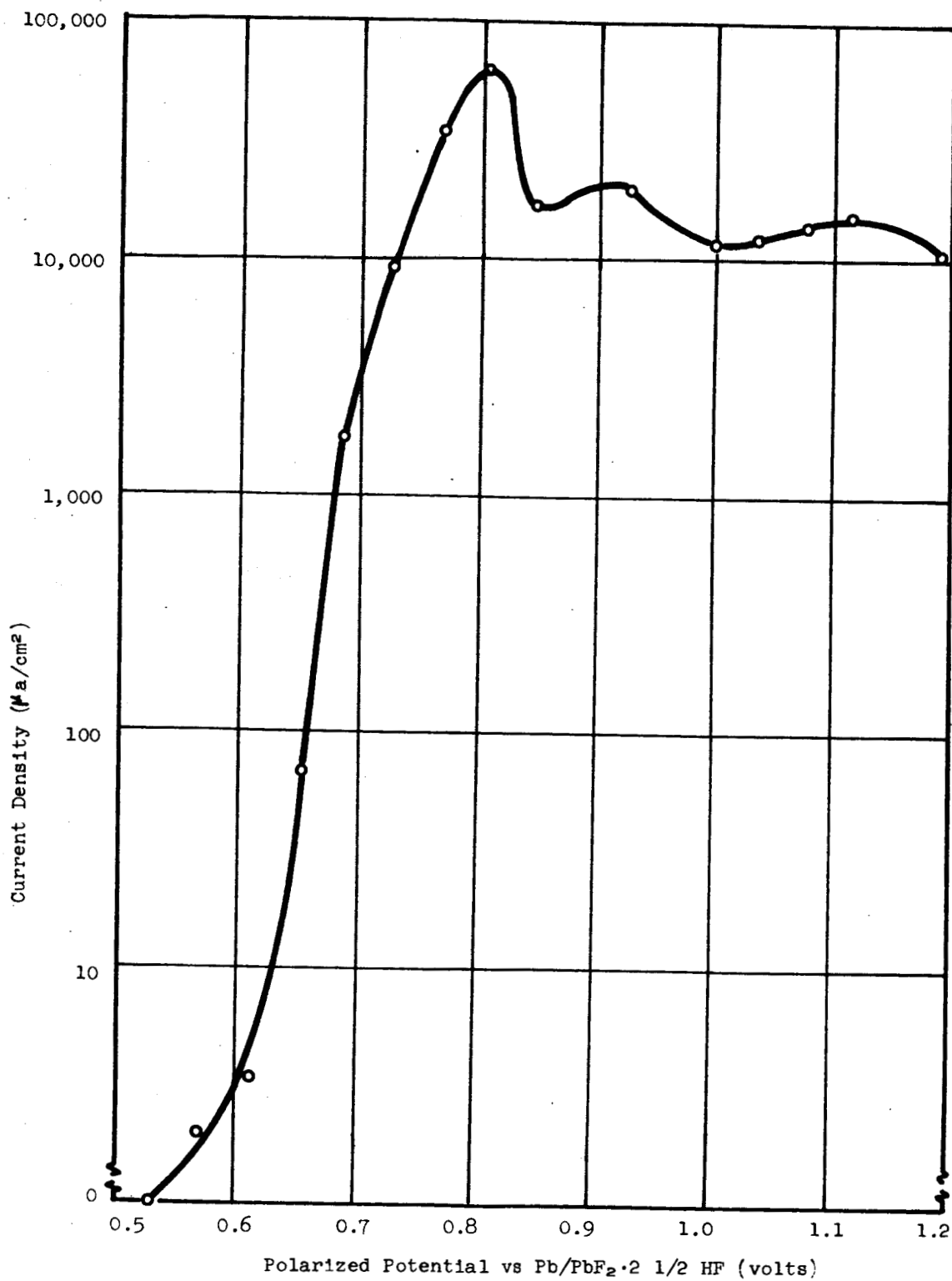


Figure 1B. Potentiostatic Anodic Polarization of Copper in KF·3HF at 85°C.

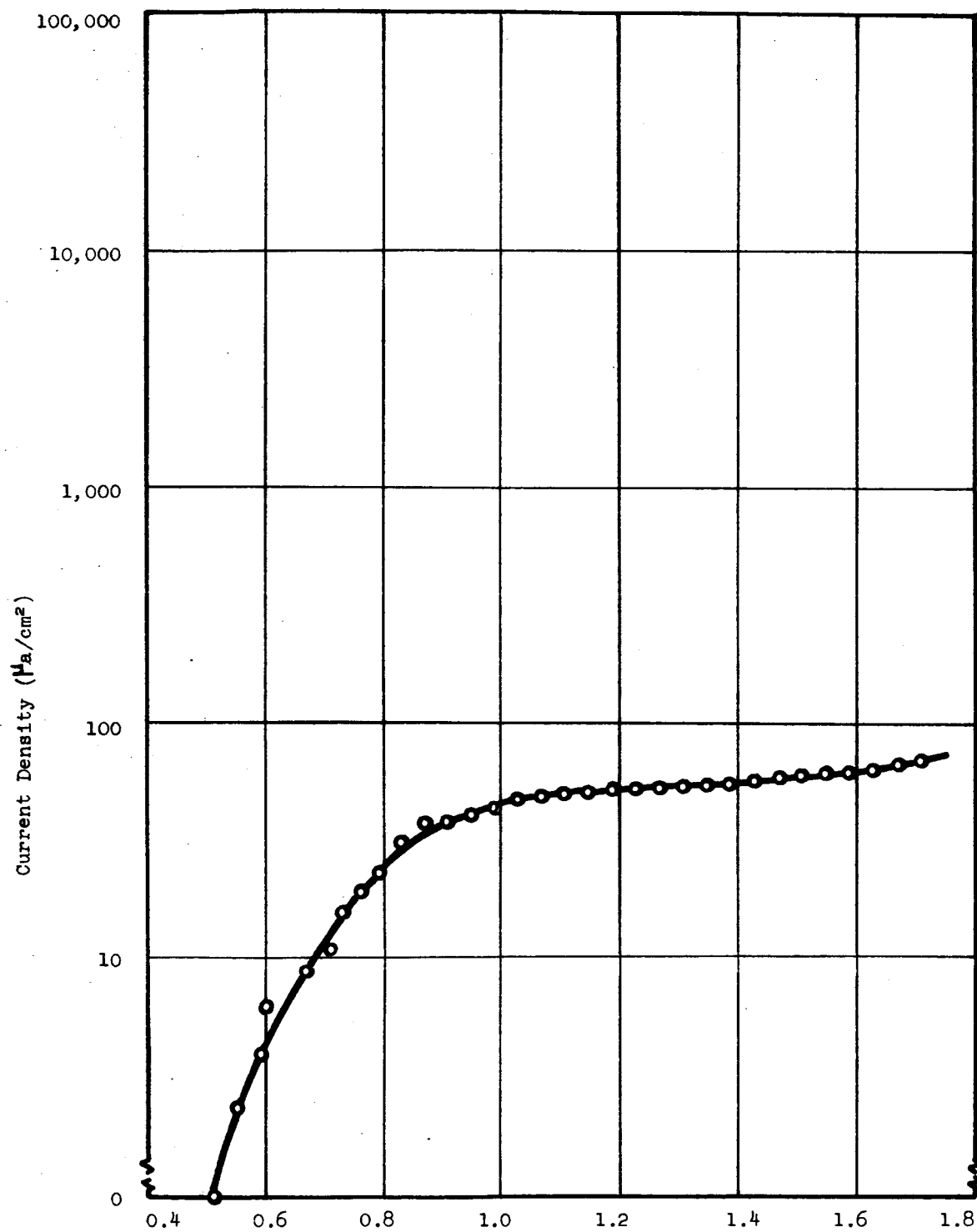


Figure 19. Potentiostatic Anodic Polarization of Solid Palladium in $KF \cdot 3HF$ at $85^\circ C$.

As contrasted to the behavior of solid nickel, the anodic current of palladium first increased as the potential became more positive and then was almost constant at about $70 \mu\text{a}/\text{cm}^2$ at potentials from 1.0 to 1.7 v to the lead-lead fluoride electrode.

2. Conclusions Regarding Metal Corrosion in $\text{KF} \cdot 3\text{HF}$ at 85°C

- (1) Solid nickel does not dissolve anodically in $\text{KF} \cdot 3\text{HF}$ at 85°C at potentials more negative than 0.3 v to the lead-lead fluoride electrode. Solid nickel is anodically protected at potentials of 0.9 to 1.6 v at a corrosion rate of about 63 milligrams of nickel per square decimeter per day (mdd) or 0.010 in. penetration per year (ipy). Solid nickel is a potential cathode material for use with chlorine trifluoride.
- (2) Highly porous nickel plaque is not anodically oxidized at potentials more negative than 0.25 v but is rapidly corroded at potentials from 0.3 to 1.6 v. The great difference between nickel plaque and solid nickel is the enormous true surface area of the former compared with the geometrical surface area on which current densities were based. The exact composition of the nickel plaque may also be different from that of the solid nickel. Nickel plaque would not be a satisfactory cathode material for use with chlorine trifluoride.
- (3) Solid copper is not anodically attacked at potentials more negative than 0.5 v, but the metal corrodes severely at potentials more noble than 0.63 v. This metal would not make satisfactory cathodes for use with chlorine trifluoride but might be used to contain the $\text{KF} \cdot 3\text{HF}$ melt in the absence of chlorine trifluoride if traces of copper can be tolerated.
- (4) Assuming that palladium dissolves as Pd^{++} , the anodic current plateau for palladium at about $70 \mu\text{a}/\text{cm}^2$ corresponds to a corrosion rate of 334 mdd or 0.040 ipy. This rather high corrosion rate would cause failure of thin palladium membranes. The potential of such anodes should be kept more negative than 0.7 v to prevent rapid dissolution. For example, at 0.7 v, a dissolution current of $11 \mu\text{a}/\text{cm}^2$ corresponds to a corrosion rate of 53 mdd or 0.006 ipy.

E. PROGRAM FOR THE SECOND QUARTER

1. Improve N_2H_4 and ClF_3 electrodes, both in $\text{KF} \cdot 3\text{HF}$ at 85°C and in HF at 0°C , by adapting flow-through and palladium diffusion systems that are compatible with the hydrogen fluoride systems.
2. Select materials of construction for use as electrodes and catalysts that are compatible with HF and ClF_3 .
3. Evaluate the efficiency of electrode processes in anhydrous HF systems.

VI. REFERENCES

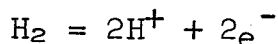
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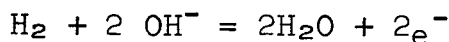
VII. APPENDIX

A. CALCULATION OF REVERSIBLE HYDROGEN POTENTIALS IN KOH SOLUTIONS

The reversible hydrogen potential for a hydrogen electrode in contact with its ions:



or the equivalent reaction in base:



versus the standard hydrogen potential (which is defined as zero at all temperatures) can be calculated for any temperature and concentration of base from the ionization constant of water, K_w , the concentration of base, and the activity coefficient of the base by the relation:

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln a_{\text{H}^+} \\ &= E^\circ - 2.303 \frac{RT}{nF} (\log K_w - \log a_{\text{OH}^-}) \text{ (ref. A-1)} \end{aligned}$$

The ionization constant of water is given as a function of the absolute temperature, T, by Harned (ref. A-2).

$$\log K_w = -4470.99/T + 6.0875 - 0.017060 T$$

Activity coefficients of potassium hydroxide solutions from Harned (ref. A-2) are plotted in Figure A-1.

For example, when $M_{\text{KOH}} = 5$, $m_{\text{KOH}} = 5.33$.

K_w and A_{OH^-} at 25°C are given in Table A-1, and the hydrogen potential versus the standard hydrogen electrode becomes:

$$E = 0 - \frac{2.303 \times 1.99 \times 298.2}{23,060} (-14.00 - 1.013) = 0.886$$

The above potential is positive according to the Electrochemical Society convention. Changing to experimental potentials, the sign of the potential is changed to minus.

Calculations of hydrogen potentials versus the saturated calomel electrode in 5M KOH at the temperatures of the experimental cells are given in Table A-1.

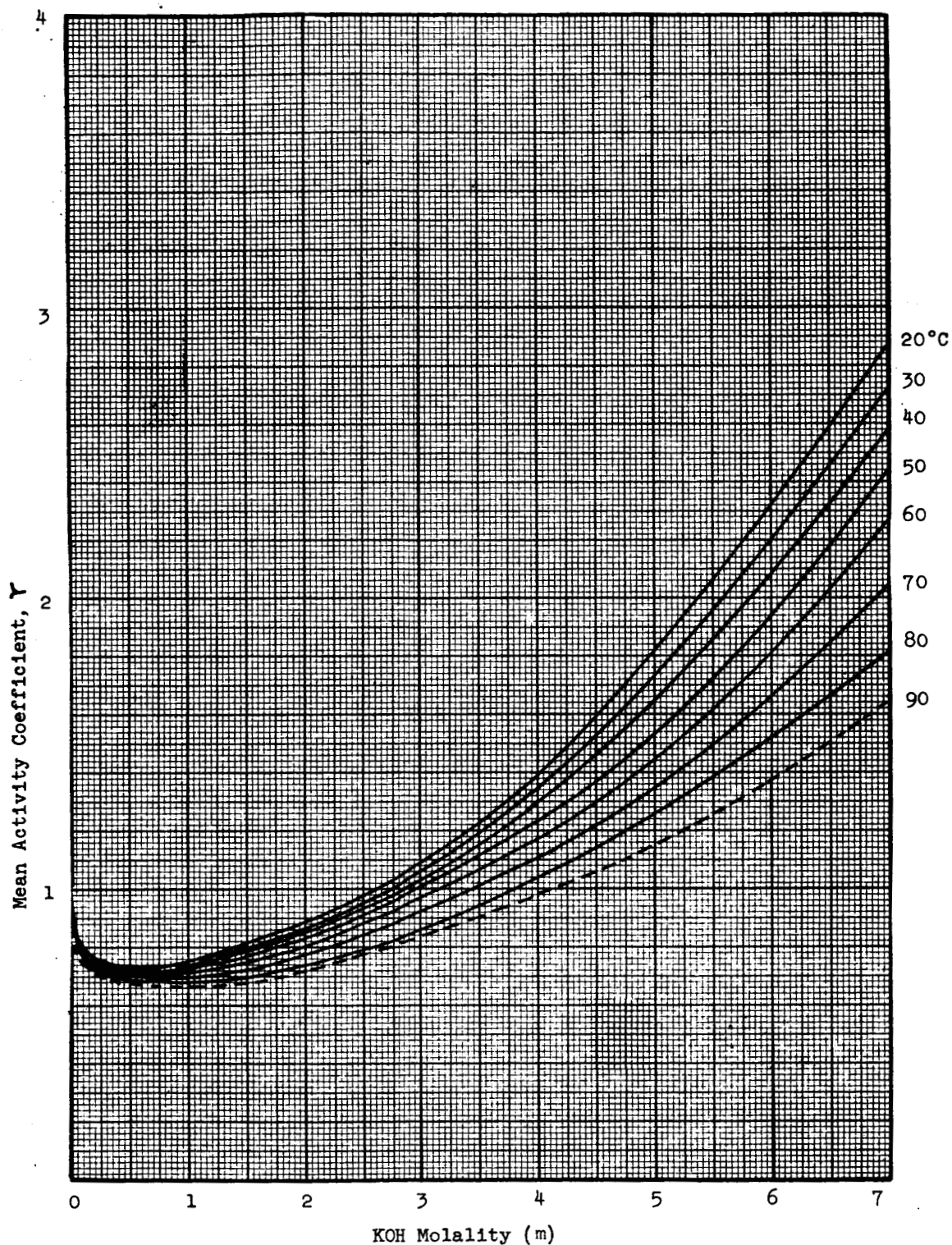


Figure A-1. Mean Activity Coefficients of Aqueous KOH Related to Concentration and Temperature. From Data of Harned (ref. A-2) (Curve for 90°C extrapolated)

Table A-1

CALCULATED DATA FOR HYDROGEN ELECTRODE POTENTIAL VS.
SCE IN 5M KOH AT 25°C, 60°C, AND 90°C

Temp. °C	$\log K_w$	RT/F	E_B° Volts	γ_{OH^-}
25	-14.00	0.0592	-0.828	1.90
60	-13.02	0.0662	-0.861	1.58
90	-12.43	0.0772	-0.900	1.23

Temp. °C	a_{OH^-}	$\log a_{OH^-}$	E_{H_2} Volts	SCE Volts	E_{H_2} vs SCE*
25	10.30	1.013	-0.886	0.24	-1.13
60	8.53	0.930	-0.925	0.22	-1.14
90	6.56	0.817	-0.958	0.20	-1.16

*Without liquid junction potential

B. REFERENCE ELECTRODE PREPARATION

1. Silver-Silver Fluoride Electrode

A piece of pure silver wire, 0.14 cm diameter by 10 cm long, was cleaned with fine emery paper (00) and anodized in $\text{KF} \cdot 3\text{HF}$ at 85°C at successively higher current densities (1, 2, 5, 10 ma/cm^2) until a polarization of 0.5 v from the original open-circuit potential occurred.

2. Lead-Lead Fluoride Electrode

A strip of pure lead 10 by 0.2 by 0.5 cm, was scraped clean with a knife and anodized in $\text{KF} \cdot 3\text{HF}$ as in (1).

3. Copper-Copper Fluoride

A strip of pure copper wire, 0.10 cm diameter by 10 cm long, was cleaned with fine emery paper and anodized in $\text{KF} \cdot 3\text{HF}$ as in (1).

4. Hydrogen-Palladium Electrode

A piece of 0.003 thick palladium, 0.5 by 1.0 cm, was spot welded to 0.05 cm diameter platinum lead wire and coated with platinum black by cathodizing in 3% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ for two minutes at 20 ma/cm^2 for each side. The electrode was washed and dried in air and cathodized in $\text{KF} \cdot 3\text{HF}$ at 5 ma/cm^2 for 60 minutes.

VIII. CONTRACT FINANCIAL STATUS REPORT

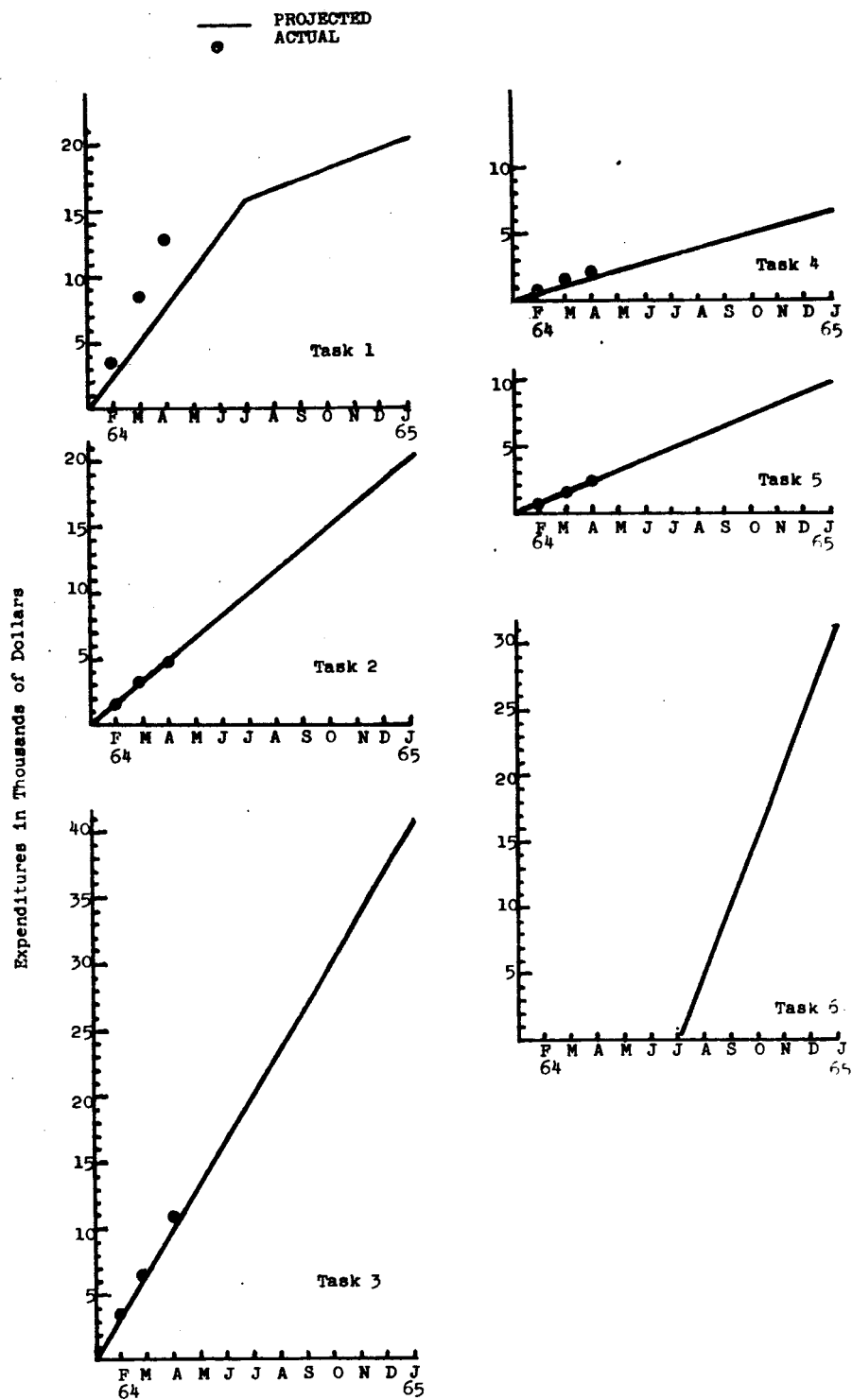
A. MANHOURS EXPENDED

April Manhours Expended
Cumulative Manhours Expended

812
2454

% of Total
(Cumulative)
Hours Expended
Per Task

<u>Task</u>	<u>Description</u>	
1	Develop anode and cathode configurations suitable for full cells and capable of scale-up to practical size (aqueous systems)	39.2
2	Continue work on non-aqueous systems (N ₂ H ₄ - HF - ClF ₃)	13.2
3	Full cell characterization-polarization data, life expectancy, shelf life, optimum operating conditions, calorimetric studies	33.5
4	Materials of construction	6.5
5	Operation of selected full cells on H ₂ -O ₂ and other specified reactants	7.6
6	Design of optimized systems to NASA requirements	--
		<hr/> 100.0



B. PROJECTED AND ACTUAL EXPENDITURES BY TASK CONTRACT NAS 3-4175

C. PERSONNEL ROSTER

<u>Name</u>	<u>Title</u>	<u>Hours Worked During April</u>
J. C. Orth	Project Leader	82
J. O. Smith	Dept. Manager	24
R. E. Chute	Research Engineer	168
S. Matsuda	Sr. Research Specialist	80
W. H. Power	Research Specialist	30
T. S. Wolanski	Sr. Mechanical Engineer	104
M. L. Cook	Technician	120
J. Him	Technician	7
G. S. Robinson	Technician	160
J. T. Sumrall	Technician	32
T. G. Linxweiler	Technical Editor	5

NEW TECHNOLOGY

Contract No. NAS3-4175

28 January 1964 to 27 April 1964

The reportable items considered to have been developed on this contract during this period are as follows:

1. Method of improving the fuel cell performance characteristics of a palladium membrane diffusion electrode by annealing at above 790°C followed by oxidizing in air at below 790°C. This is considered possibly a patentable invention.
2. Method of catalyzing the electrolyte side of a palladium membrane diffusion electrode by plating with rhodium and oxidizing (by heating in air) to provide rhodium oxide and palladium oxide at the surface. This is considered an invention, possibly as a species of a broad invention of varying the properties of palladium membrane diffusion electrodes by introduction of different valency cations into a surface PdO layer so as to alter the ratio of electron deficits to cation vacancies. A patent disclosure is in preparation.
3. A selective catalyst system for a hydrazine/nitric acid fuel cell, with Pt-catalyzed carbon as the anode and carbon as the cathode. This is considered probably unpatentable, though novel.
4. Electrochemical systems using ClF_3 as oxidizer, and metal (especially Pb) anodes with an HF electrolyte such as a $\text{KF} \cdot 3\text{HF}$ melt. This is considered patentable, as a specific embodiment of the ClF_3 fuel cells disclosed in the previous final report on Contract No. NAS3-2791.

The above-described developments are disclosed in full detail in the Quarterly Report No. 1 on the above-identified contract, covering the period 28 January to 27 April 1964.